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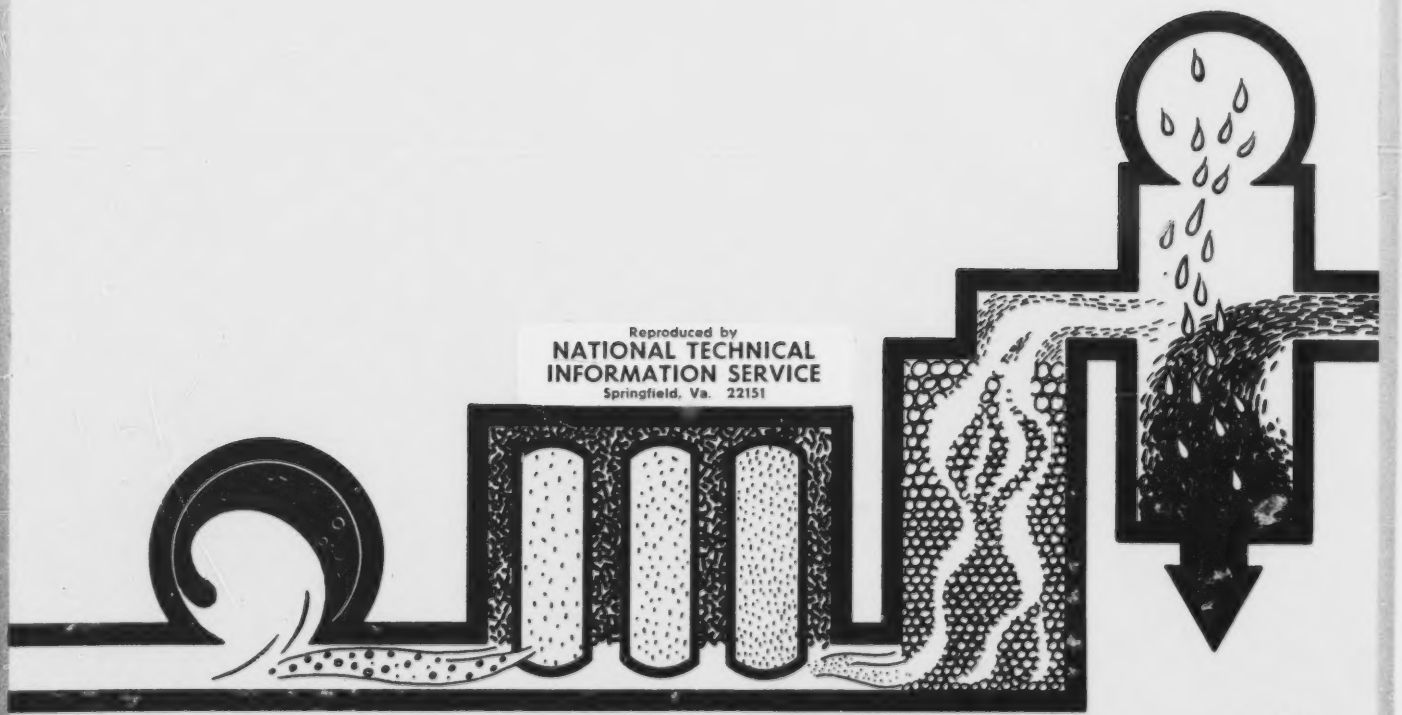

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SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No. 2. 3. Accession No. W 72-09383

4. Title WASTEWATER AMMONIA REMOVAL BY ION EXCHANGE

5. Report Date
6.
8. Performing Organization Report No.

7. Author(s) [redacted]

9. Organization Battelle-Northwest, Richland, Washington

10. Project No. EPA 17010 ECZ 02/71 (Program no. 17010 EGZ.)
11. Contract/Grant No. [redacted]
13. Type of Report and Period Covered

12. Sponsoring Organization Environmental Protection Agency

15. Supplementary Notes (Water Pollution Control Research Series [redacted], February 1971, 113 p, 20 fig, 3 tab, 5 ref.

16. Abstract> Pilot plant investigations of a nitrogen removal system employing a natural zeolite, clinoptilolite, which is selective for ammonium ions in the presence of sodium magnesium, and calcium ions, were conducted at the South Tahoe Public Utility district. The system was operated on both clarified and carbon treated secondary effluent and clarified raw sewage. 94% removal was the average ammonia removal obtained using Tahoe tertiary effluent with single 6 ft. deep beds. With two column semi-countercurrent operation, 97% ammonia removal was achieved with 4.7 ft. deep beds, operating to an average of 250 bed volumes. For clarified raw sewage treated in the semi-countercurrent columns, 93% average ammonia removals were achieved at average throughputs of 232 bed volumes. Regeneration was accomplished by reacting the exhausted zeolite with hydroxyl ions to form an alkaline aqueous ammonia solution suitable for air stripping and discharge to the atmosphere. The regenerant solution is not discarded and no liquid wastes are generated. A 7 1/2 mgd plant was designed based on the pilot plant data. Estimates for operational costs and construction costs, based on current costs in the Lake Tahoe region and capital costs amortization at 6% over 20 years were $84.95/million gallons and $63.10/million gallons, respectively. (Lowry-Texas)

17a. Descriptors *Ammonia, *Ion exchange, *Zeolites, Resins, Separation techniques, Nitrogen, Lime, Pilot plants, Design criteria, Construction costs, Cost analysis, Hydrogen ion concentration, *Waste water treatment

17b. Identifiers *Clinoptilolite, *Regeneration, South Lake Tahoe (Calif)

Copy available from GPO Sup Doc [redacted], $1.25; microfiche from NTIS as PB 209 854. $1.95.

17c. COWRR Field & Group 05D

18. Availability

19. Security Class. (Report)
20. Security Class. (Page)
21. No. of Pages
22. Price

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WATER RESOURCES SCIENTIFIC INFORMATION CENTER
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WRSIC 102 (REV. JUNE 1971)

WASTEWATER AMMONIA REMOVAL BY ION EXCHANGE

Mobile Pilot Plant Studies and Process Design with Electrochemical Renovation of Regenerant

by

Battelle-Northwest
Richland, Washington 99352
Project #17010 ECZ
Contract #14-12-579

Process Design with Air Stripping Renovation of Regenerant

by

South Tahoe Public Utility District
South Lake Tahoe, California 95705
Project #17010 EEZ
Contract #14-12-561

for the

ENVIRONMENTAL PROTECTION AGENCY

February 1971

1.25

EPA Review Notice

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ABSTRACT

Pilot plant investigations were conducted on the ion exchange removal of ammonia-nitrogen from clarified and carbon-treated secondary effluents and from clarified raw sewage. The ion exchange process utilized clinoptilolite, a natural zeolite. Average ammonia removals from low magnesium wastewaters were in the range of 93% to 97%. With a wastewater Mg concentration of 20 mg/l, solids formation presented problems but they appear surmountable. The primary method used for regenerant renovation was air stripping with which a 2N regenerant at a pH of 11.5 is recommended. Electrolytic regenerant renovation using a neutral solution that is less prone to solids formation was also piloted during the project.

Two process designs are included giving cost estimates for ion exchange ammonia removal from tertiary effluent. With capital costs amortized at 6% for 20 years, the total cost to remove ammonia from 1000 gal. of tertiary effluent is 14.8¢ for a 7.5 mgd plant using regenerant air stripping and 12.7¢ for a 10 mgd plant using electrolytic regenerant renovation. The 7.5 mgd design was prepared by South Tahoe Public Utility District under EPA Project Number 17010 EEZ and is included for convenience. Other work discussed in the report was performed by Battelle-Northwest under EPA Project Number 17010 ECZ.

This report was submitted in fulfillment of Project Number 17010 ECZ, Contract 14-12-579, under the sponsorship of the Water Quality Office, Environmental Protection Agency.

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SUMMARY AND CONCLUSIONS

1. The selective ion exchange process for ammonia nitrogen (commonly called ammonia) removal from wastewater is believed to be best suited for use in those areas which experience prolonged periods of freezing weather during winter and where very high degrees of removal must be consistently maintained. Other processes such as air stripping[1] alone and biological nitrification-denitrification[2] may be used in warm climates at a lower cost but at somewhat lower efficiency.

2. Process designs provided costs for two alternate ion exchange methods of ammonia removal from tertiary effluent. From a Battelle design utilizing electrolytic regenerant renovation (this project), the cost per thousand gallons was 9.04¢ for operating costs and 3.64¢ for 20 year-6 percent capital amortization giving a total cost of 12.7¢/1000 gal. From a South Tahoe Public Utility District design utilizing air stripping for regenerant renovation, the cost per thousand gallons was 8.5¢ for operating costs and 6.3¢ for 20 year-6 percent capital amortization with a total cost of 14.8¢/1000 gal. South Tahoe's design was developed under WQO/EPA Contract No. 14-12-561 and their report is Appendix C in this present report. The lower capital cost of the Battelle design was due to use of reinforced concrete tanks for the ion exchange beds instead of the steel pressure vessels specified by South Tahoe. Concrete tanks of simplified design can be used with neutral electrochemical renovation because solids precipitation is a lesser problem and backwashing and cleanout need not be provided for.

3. The ion exchange process concentrates the ammonia in an easily processed, relatively small volume of liquid regenerant. Disposal of ammonia to the atmosphere by air stripping the regenerant is acceptable in most areas because prevailing winds move the ammonia over land surfaces where the ammonia is adsorbed by the soil during periods of precipitation. It would be practical to heat the small volume of regenerant for stripping in cold weather. In those areas where atmospheric disposal is not satisfactory, the ammonia can be destroyed by electrolysis of the regenerant. Electrolysis of the regenerant produces chlorine which reacts with the ammonia to produce nitrogen gas.

4. An average ammonia removal of 94% was obtained with single 6 ft. deep beds operating to 150 bed volumes with Tahoe tertiary effluent. With two column semi-countercurrent operation, 97% ammonia removal was achieved with 4.7 ft. deep beds operating to an average of 250 bed volumes throughput. When clarified raw sewage was treated by the two column semi-countercurrent operation, ammonia removal averaged 93% with average throughputs of 232 bed volumes.

5. Batch regeneration by recirculating 4 bed volumes of 1 M $CaCl_2$, 0.2M NaCl and pH 11.5 (adjusted with lime) solution appears to minimize regenerant volume. However, a wide range of concentrations was not investigated and steady-state conditions may not have been reached. The regenerant was chosen to include: (1) significant Na which has been found to lengthen the service cycle and shorten the elution cycle; (2) 1M (2N) Ca concentration to provide for high elution capacity and approximate what would be expected with continued lime pH adjustment in service; and (3) high pH to shift the equilibrium toward NH_3 production to facilitate air stripping. Further optimization of the regenerant composition may result from experience. Wasting of regenerant may be necessary if undesirable build-up in concentration occurs. On the other hand, considerable salt addition may be necessary due to dilution of the regenerant during use. Allowances for NaCl and lime additions used in the designs discussed in this report may have to be adjusted.

6. Processing of wastewaters with high Mg^{+2} concentrations may require clarification of the regenerant to avoid plugging the bed with $Mg(OH)_2$. Additional work is needed to verify this approach.

7. Processing of clarified and filtered raw sewage appears to cause some biological growth in the zeolite beds but is adequately removed during the regeneration cycle.

8. Zeolite attrition was 0.17% per cycle when using high pH regeneration due to backwashing required for solids removal. Attrition would be very low for the neutral regeneration proposed with electrochemical regenerant renovation. Under neutral conditions much less solids would form and high rate backwashing would be unnecessary. Zeolite ammonia capacity does not change significantly with service.

9. Pilot studies demonstrated that air stripping of regenerant is practical. The calcium carbonate scale formed on the stripping column packing did not interfere with the stripping efficiency for operating periods up to 65 days. The physical character of the scale varied from flaky to hard. Water spraying removed the flaky scale to a large degree, but water fluidization of the packing was required for removal of the hard scale.

10. Laboratory studies and preliminary pilot studies demonstrated the feasibility of electrochemical renovation of regenerant. The electrical energy required to remove one gram of NH_3-N varied from 35-54 watt hours. White scale formation occurred on the cell cathode. This is expected to be minimized, however, by promoting turbulence in the cell with baffles or other cell modifications.

RECOMMENDATIONS

Further development of the electrochemical method of removing the ammonia from the spent regenerant is recommended. The major advantages of this approach relative to that of air stripping of the spent regenerant are:

1. No precipitation occurs in the zeolite bed during regeneration because neutral solutions are used,

2. No atmospheric disposal of ammonia is necessary,

3. Overall scaling problems associated with the use of lime are eliminated.

Preliminary cost studies indicate that electrochemical renovation of spent regenerant will be competitive with air stripping renovation.

The development program recommended for electrochemical treatment of spent regenerant from the selective ion exchange process should include studies to determine electrode life, and optimum current density, pH, salt concentration and temperature. Methods to control calcium and magnesium hydroxide scaling on the cathode should be evaluated to minimize cell resistance.

INTRODUCTION

The results of laboratory and initial pilot plant studies on ammonia removal by selective ion exchange have been reported previously[3,4]. A naturally occurring zeolite, clinoptilolite, is employed as the ion exchange medium which preferentially sorbs ammonium ions in the presence of sodium, calcium, and magnesium ions. The zeolite can be regenerated with solutions containing high concentrations of calcium ions. Spent regenerant solutions can be renovated for reuse by air stripping or electrolysis to remove ammonia. Basically, the selective ion exchange process concentrates the ammonia into a relatively small volume of liquid (regenerant) which can be: (1) air stripped even in cold weather using low heat input to prevent freezing and to maintain high ammonia removal efficiency; or (2) electrolyzed to convert the ammonia into innocuous nitrogen gas.

Consistently high ammonia removals from clarified trickling filter effluent were previously demonstrated in the laboratory[4]. The ammonia removals varied from about 95% for a single zeolite bed with an output of 150 bed volumes to more than 99% removal for two beds in semi-countercurrent series operation with an output of 200 to 300 bed volumes.

The main objective of this program is demonstration of the use of the selective ion exchange process on an engineering scale for removing ammonia from a variety of wastewaters. A 100,000 gpd mobile pilot plant was employed in this effort which included operations at the South Tahoe Public Utility wastewater treatment plant at South Lake Tahoe, California; the Pomona Wastewater Treatment Plant at Pomona, California; and the Joint WQO-DC Pilot Plant at Blue Plains in Washington, D. C. Wastewaters encountered in the pilot plant studies include clarified (Pomona) and carbon treated (Tahoe and Pomona) activated sludge plant effluents and clarified raw sewage (Blue Plains).

The above demonstration sites were selected to give a wide range in dissolved organic concentrations and dissolved salts concentrations, particularly magnesium salts. The dissolved organics may foul the zeolites directly or indirectly by supporting biological growths which cover the zeolite particles. Magnesium precipitates in the zeolite bed during regeneration with lime and may cause operational problems where the concentration is high.

Two process designs have been developed for zeolite ammonia removal from tertiary effluent. During the present Battelle project, a 10 mgd plant utilizing electrochemical renovation of the regenerant was designed. This design paralleled one developed earlier for a 7.5 mgd plant using regenerant air stripping by the South Tahoe Public Utility District under WQO/EPA Contract No. 14-12-561. The 10 mgd Battelle design is Appendix B in this present report and the South Tahoe project report is included as Appendix C.

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PILOT PLANT OPERATION

The mobile pilot plant used in these studies has been described previously[4]. The water treatment unit (Recla-Mate SWB tertiary sewage treatment plant manufactured by Neptune MicroFloc, Incorporated, of Corvallis, Oregon) was not used for the most part because clarified water was available at the demonstration sites. The 39 in. diameter ion exchange vessels were converted from 750 gallons capacity to 500 gallons capacity by leaving off the top sections. This reduction in size greatly facilitated assembly and disassembly of the ion exchange vessels by eliminating the use of a crane to lift the top section to and from the roof of the trailer. The 500 gallon capacity was entirely satisfactory for the demonstration program. A flow diagram for the selective ion exchange process is illustrated in Figure 1 and a photograph of the mobile pilot plant in operation at South Lake Tahoe is given in Figure 2.

The stripping tower packing consisted of 1 in. polypropylene Intalox(R) saddles for ease in removal and repacking. Column diameter was 43 in. and packing depth was 7 ft.

Electrochemical renovation of regenerant involved the use of two 500 amp electrolysis cells (manufactured by Pacific Engineering and Production Company of Henderson, Nevada). The electrolysis cell consists of a lead dioxide coated graphite anode, 4 1/4 in. diameter by 45 in. long, placed in a copper can that serves as the cathode.

The feed streams were pumped downflow through either a single zeolite bed or two beds in series. Regenerant solutions were pumped upflow through the beds at rates sufficient to remove precipitated or filtered solids from the beds. During semi-countercurrent operation, which permits greater utilization of the available ion exchange capacity, the loaded zeolite bed (first in series) was removed from service for regeneration while a freshly regenerated bed was placed at the end of the series.

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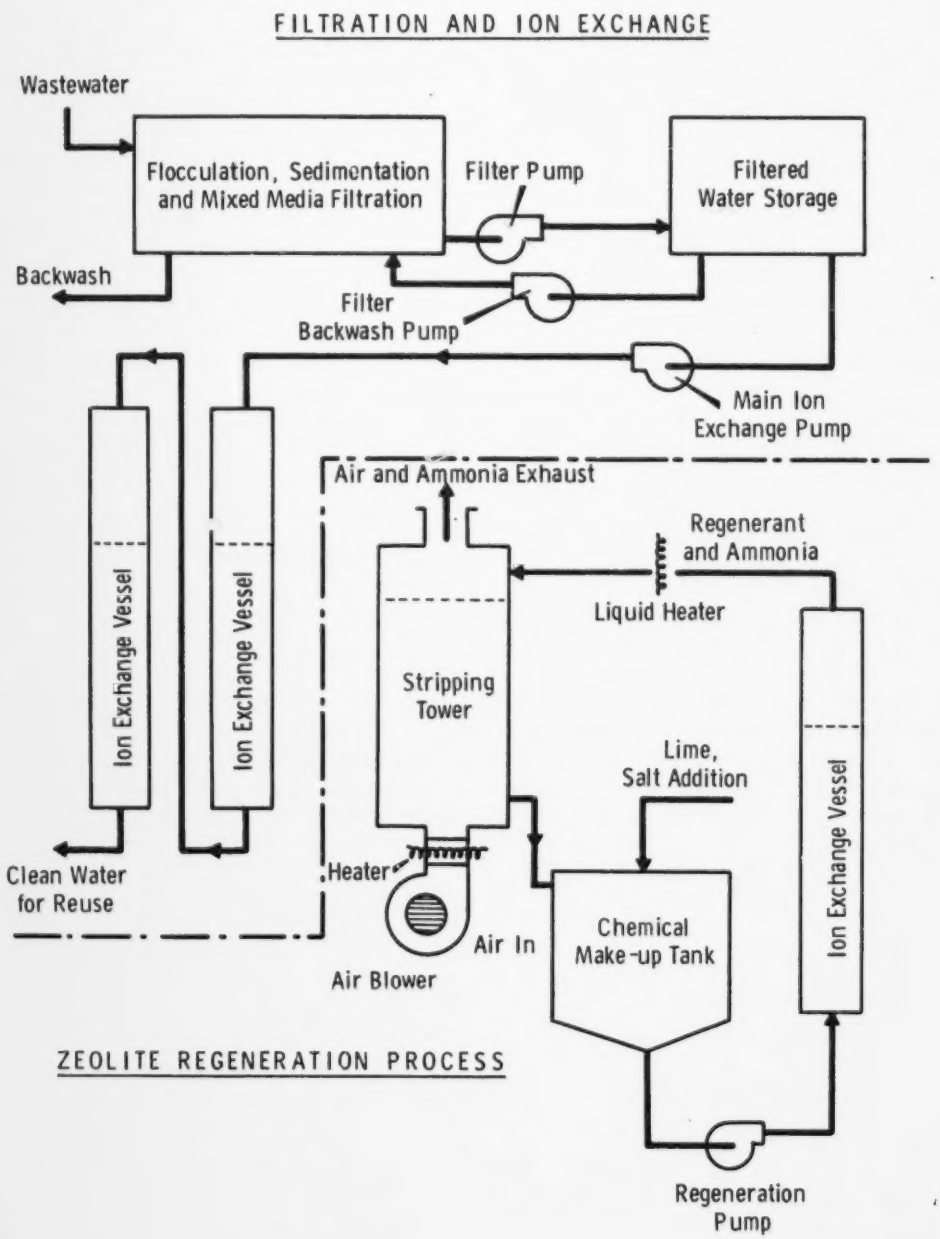

FIGURE 1. FLOWSHEET FOR AMMONIA SELECTIVE ION EXCHANGE PROCESS

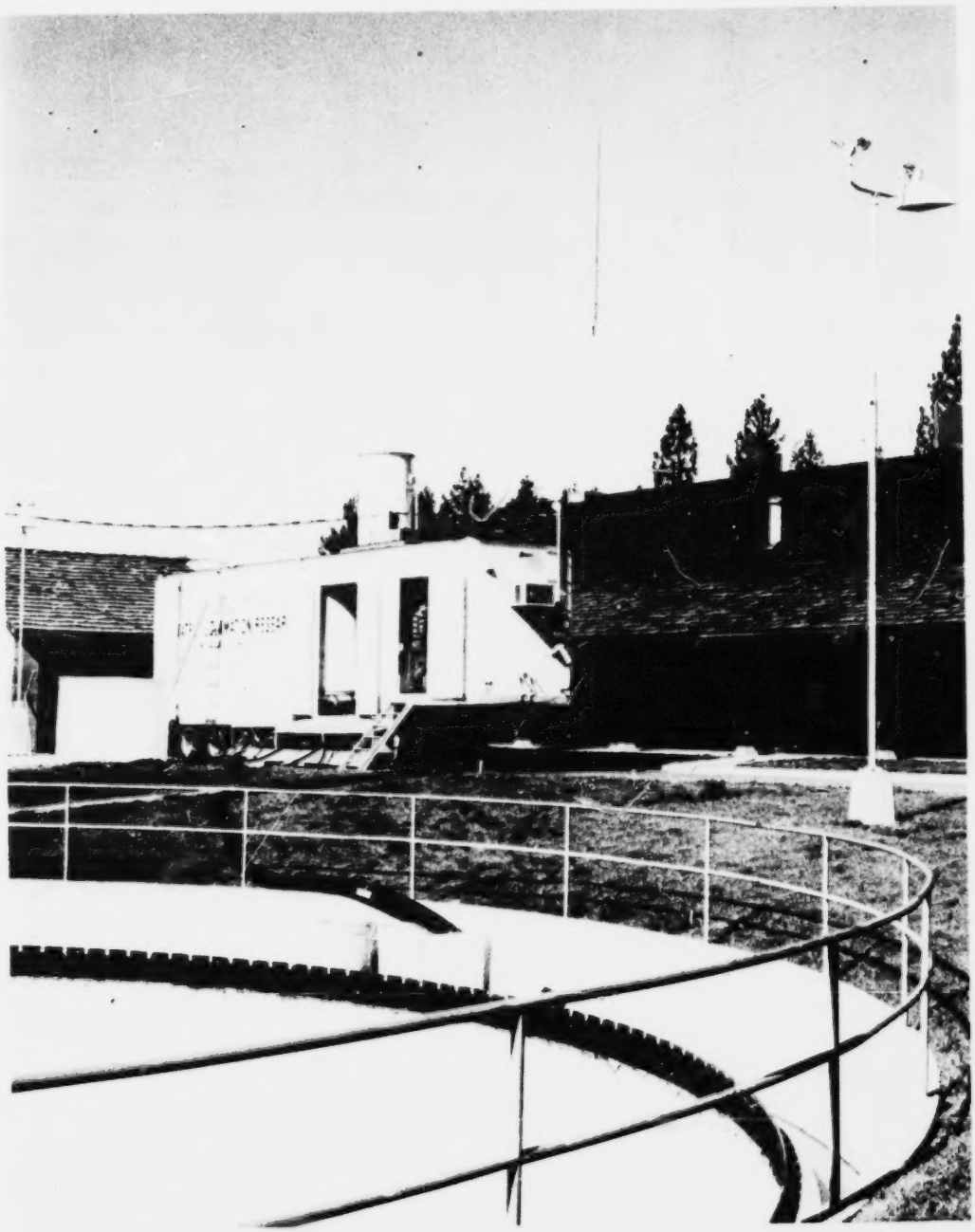

FIGURE 2. PHOTOGRAPH OF MOBILE PILOT PLANT IN OPERATION AT SOUTH LAKE TAHOE

ION EXCHANGE EQUILIBRIA

The ion exchange equilibria for the systems NH_4^+-Na^+, NH_4^+-K^+, NH_4^+-Ca^{+2} and NH_4^+-Mg^{+2}, with clinoptilolite and other zeolites, have been reported by Ames[3]. The original data reported by Ames has been extended to include higher Ca^{+2}: NH_4^+ and Na^+: NH_4^+ ratios. Plots of the NH_4^+ selectivity coefficients (defined in Appendix A) vs. the solution concentration ratios of the cations are shown in Figures 3 and 4. This additional data is useful for computing the equilbria in regenerant solutions. However, standard solutions of 0.1N were used in obtaining the data. Corrections for activity differences were needed to improve accuracy when using the data in Figures 3 and 4 to predict maximum wastewater ammonia loadings on clinoptilolite. An example of the computation is given in Appendix A.

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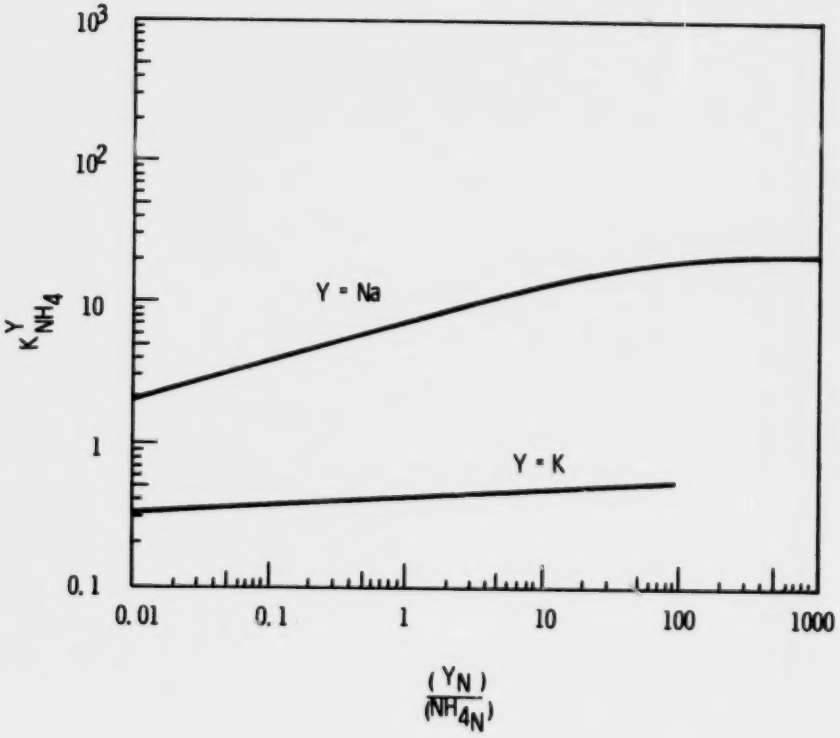

FIGURE 3. SELECTIVITY COEFFICIENTS VS. CONCENTRATION RATIOS OF SODIUM OR POTASSIUM AND AMMONIUM IN THE EQUILIBRIUM SOLUTION WITH HECTOR CLINOPTILOLITE AT 23°C FOR THE REACTION $(Y)_Z + (NH_4)_N = (NH_4)_Z + Y_N$

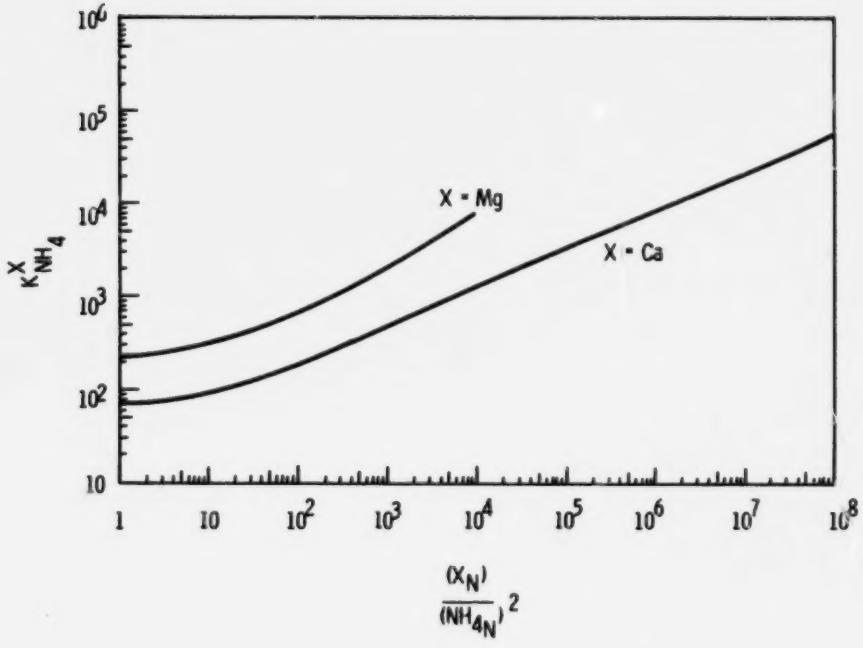

FIGURE 4. SELECTIVITY COEFFICIENTS VS. CONCENTRATION RATIOS OF CALCIUM OR MAGNESIUM AND AMMONIUM IN THE EQUILIBRIUM SOLUTION WITH HECTOR CLINOPTILOLITE AT 23°C FOR THE REACTION $(X)_Z + 2(NH_4)_N = 2(NH_4)_Z + X_N$

Single Column Loading Studies

Column loading studies were carried out to establish the volume of feed water that can be processed through a zeolite bed until significant ammonia breakthrough occurs. The typical composition of the various feed streams employed in these studies are listed in Table 1.

TABLE 1

TYPICAL COMPOSITION OF FEED STREAMS

	Activated Sludge Plant Effluent		Clarified Raw Sewage
	Tahoe Carbon Treated	Pomona*	Blue Plains
NH_3-N mg/liter	15	16	12
Na mg/liter	44	120	35
K mg/liter	10	18	9
Mg mg/liter	1	20	0.2
Ca mg/liter	51	43	30
pH			
Range	7-8	6.5-8.2*	7-9
Avg.	7.4	6.9, 7.8*	7.9
COD	11	10	50
TDS	325	700	250

*NOTE: Approximately half of the runs at Pomona were made with carbon treated secondary and the others with alum coagulated secondary. The average pH of the carbon column effluent was 7.8 and the average pH of the alum coagulated secondary was 6.9.

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The equilibrium NH_3-N bed loading computed for each of the wastewaters listed in Table 1 is 4.1 g/l, 3.9 g/l, and 4.3 g/l, respectively, for Tahoe, Pomona, and Blue Plains. Figure 5 presents equilibrium bed loading in an alternate way. The minimum bed volumes required to attain equilibrium NH_3-N loading are expressed as a function of the NH_3-N concentration in the wastewater with the concentrations of metal ions held constant. For actual operation, the bed volume values given in Figure 5 will normally represent the 50 percent breakthrough point where the effluent concentration is 50% of the feed concentration.

Tahoe and Blue Plains column loading data are given below. However, Pomona loading data are thought to be atypical because of magnesium hydroxide formation during regeneration, and are not reported here. Ways of dealing with the magnesium hydroxide solids were investigated at Pomona but time did not permit obtaining loading data under realistic operating conditions. The Pomona work is discussed in the section on Regeneration Studies.

Ammonia breakthrough curves for a single 6 ft deep bed of clinoptilolite are illustrated in Figure 6 for Tahoe tertiary effluent with flow rates varying from 6.5 to 9.7 bv/hr (bed volumes per hour) with 15 to 17 mg/l NH_3-N in the feed stream. A throughput value of 150 bed volumes is recommended for design. The average NH_3-N concentration of the total effluent to that point would be about 1 mg/l or less. Follow up breakpoint chlorination would probably be more effective for removing the residual, if required, than greater ion exchange column throughputs.

The average concentration for each curve is obtained by integrating under the curve. Curve 1 at 8.1 bv/hr has the lowest average effluent NH_3-N concentration (0.67 mg/l) for 150 bed volumes, but it also has the lowest average influent NH_3-N concentration (15 mg/l). Curve 2, at 6.5 bv/hr, has an average of 0.83 mg/l NH_3-N in 150 bed volumes of effluent with an influent containing 17 mg/l NH_3-N. Curve 3, at 9.7 bv/hr, has an average effluent NH_3-N concentration of 1.2 mg/l and high initial NH_3-N leakage, which is due to insufficient backwash removal of residual lime remaining in the bed after regeneration. The effluent pH for Curve 3 was 10.4 at the time of the first sample. Since the ammonia is poorly ionized at high pH, the ion exchange sorption decreases and effluent NH_3-N was high until the residual lime washed out. In spite of this, NH_3-N removals for 150 bed volume throughputs averaged 94% over the three runs.

Exchange due to the 150 bed volume throughput value selected to maintain an average NH_3-N concentration at or below 1 mg/l uses only 55 to 58 percent of the zeolite's equilibrium capacity. The number of bed volumes throughput per bed can be increased while maintaining low NH_3-N effluent concentrations with semi-countercurrent operation. This type of operation using two beds will be discussed later.

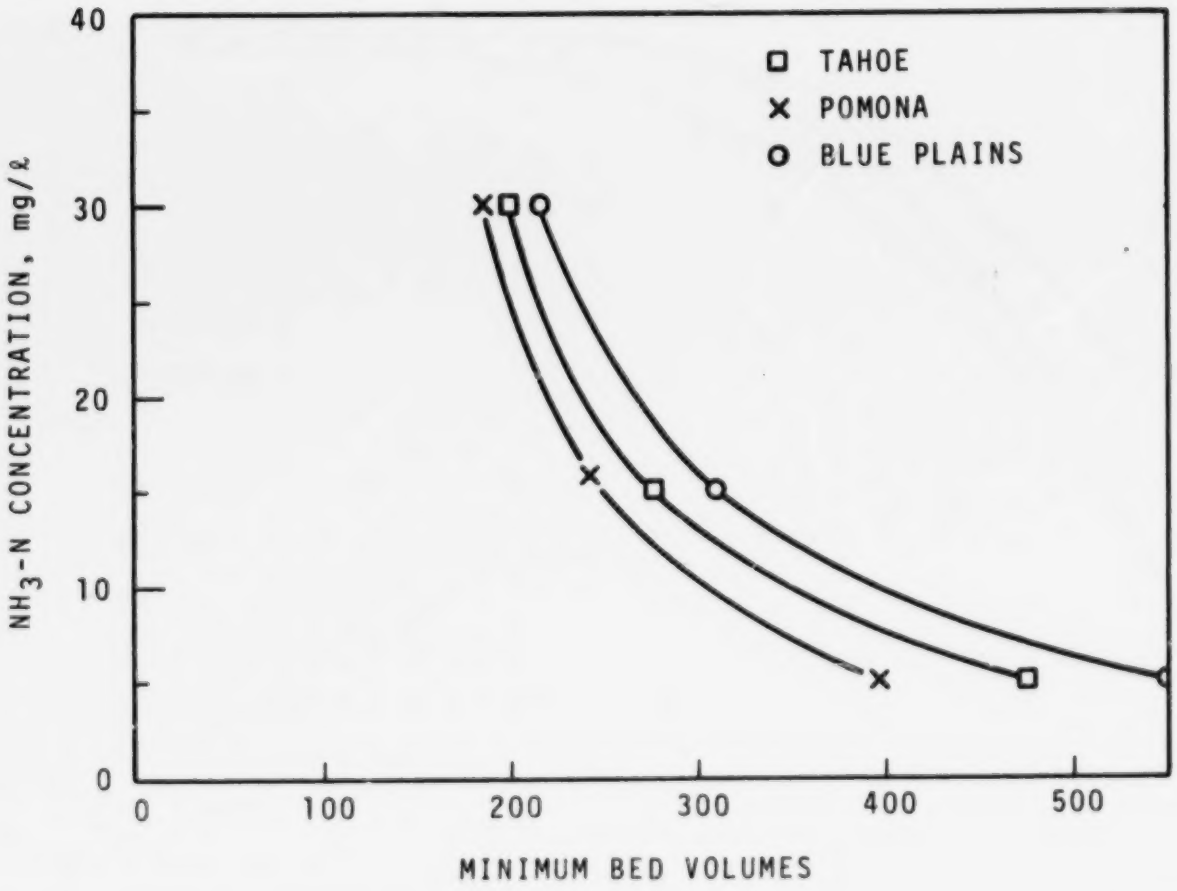

FIGURE 5. MINIMUM BED VOLUMES AS A FUNCTION OF NH_3-N CONCENTRATION

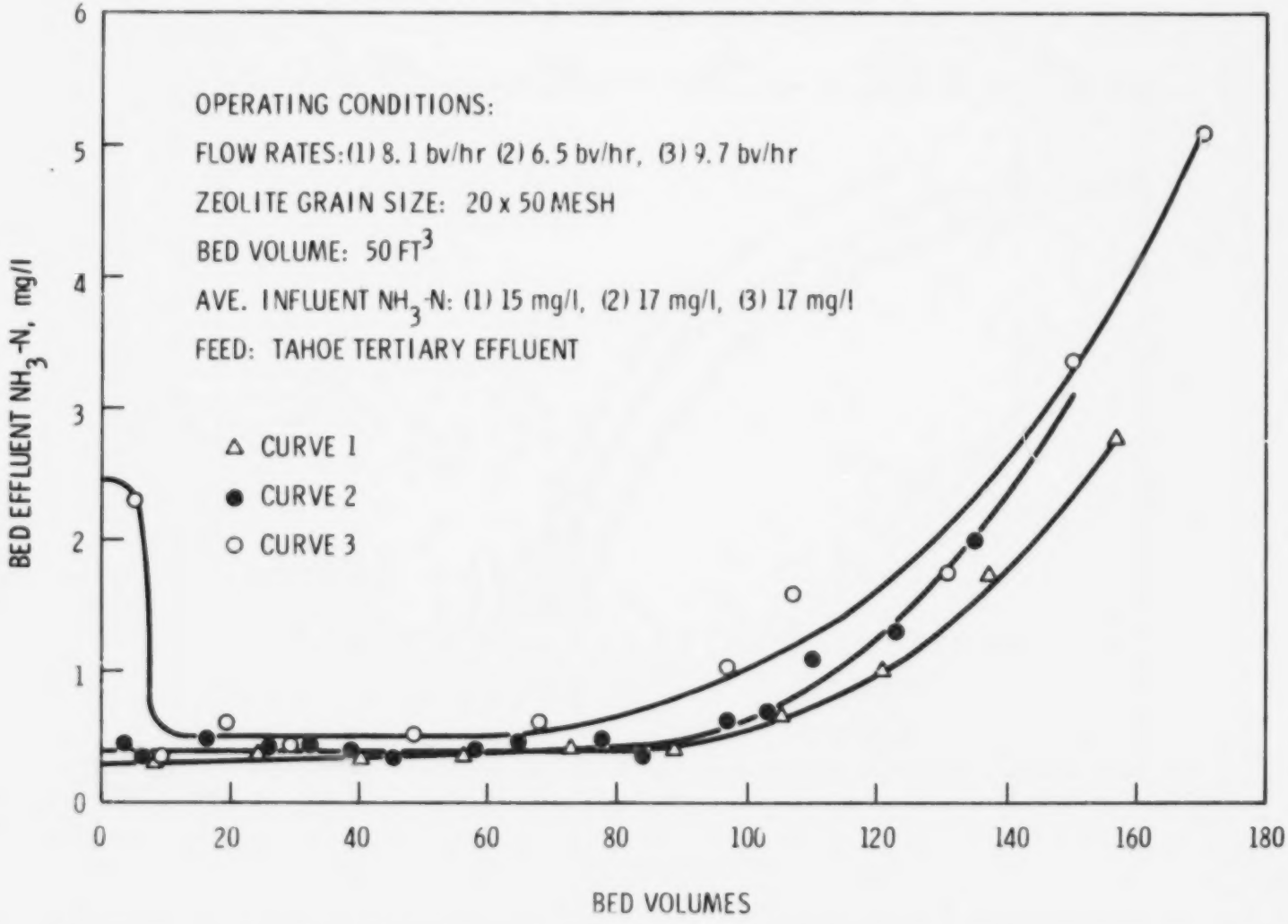

FIGURE 6. AMMONIA BREAKTHROUGH CURVES FOR A 6 FT CLINOPTILOLITE BED AT VARIOUS FLOW RATES

The effect of bed depth at a flow of 4.8 gpm/ft^2 is illustrated in Figure 7. Two 4.5 ft deep zeolite beds were run in series to provide simultaneous data on 4.5 ft and 9 ft bed depths. The average NH_3-N concentration in 150 bed volumes of effluent from the first bed in series (Curve 2, 4.5 ft bed depth) was 0.81 mg/l at a flow rate of 8.4 bv/hr. The average NH_3-N concentration in the effluent from the second zeolite bed (Curve 1, 9 ft total bed depth) was 0.35 mg/l at a flow rate of 4.2 bv/hr. The average NH_3-N concentration in the influent was 12 mg/l.

The effect of bed depth on ammonia breakthrough with two separate columns at 9.7 bv/hr in each case is illustrated in Figure 8. Curve 3 from Figure 6 for a 6 ft bed, and discussed previously, is repeated and shown with data from a 3 ft bed. In general, the shallow bed of clinoptilolite was not as effective for ammonia removal as the deep bed at the same bed volume flow rate. The shallow bed has a lower flow velocity which may lead to easier plugging of portions of the screen or bed by lime or precipitated solids. Plugging would cause poor flow distribution and lower bed efficiency.

Two Column Semi-Countercurrent Operation

Several beds in series can be operated more effectively if a column is removed from the influent end when it becomes loaded while simultaneously adding a regenerated column at the effluent end. This procedure moves zeolite beds countercurrent to liquid flow. Beds can be loaded nearer to capacity with this procedure than with single column or parallel feed multi-column operation. The most highly loaded column is always at the influent end backed up by one (if two in series) or more columns having decreasing loadings and NH_3-N concentrations at locations progressively nearer the end of the series. Removal of a column is not decided by applying a breakthrough criterion to the column's own effluent but by breakthrough at the end of the series.

The performance was evaluted for countercurrent operation of three columns (two on stream while regenerating the third). Performance data for six runs with two columns in series are listed in Table 2 for operations at Tahoe. The average ammonia nitrogen concentration in the effluent from the six runs was 0.43 mg/l, and the average influent volume processed through each column was 250 column volumes. The ion exchange columns each contained 4.7 ft deep beds with 39 ft^3 of 20 x 50 mesh clinoptilolite. The average influent ammonia nitrogen for each run varied from 10.3 mg/l to 16.1 mg/l, and the second column effluent varied between 0.38 mg/l and 0.66 mg/l ammonia nitrogen. The low and high effluent values were obtained with the low and high influent values, respectively. Loading on the first columns in series was terminated when the effluent from the second columns reached 1-2 mg/l ammonia nitrogen. Typical breakthrough curves for the first and second columns in series with Tahoe tertiary effluent are illustrated in Figure 9 for an average influent ammonia nitrogen concentration of 15.1 mg/l. Ammonia loadings were increased from an average of 57% to an average of 85% of equilibrium capacity by going from single bed to series operation; however, the piping necessary for this is more complicated. Ammonia nitrogen removals averaged 97%.

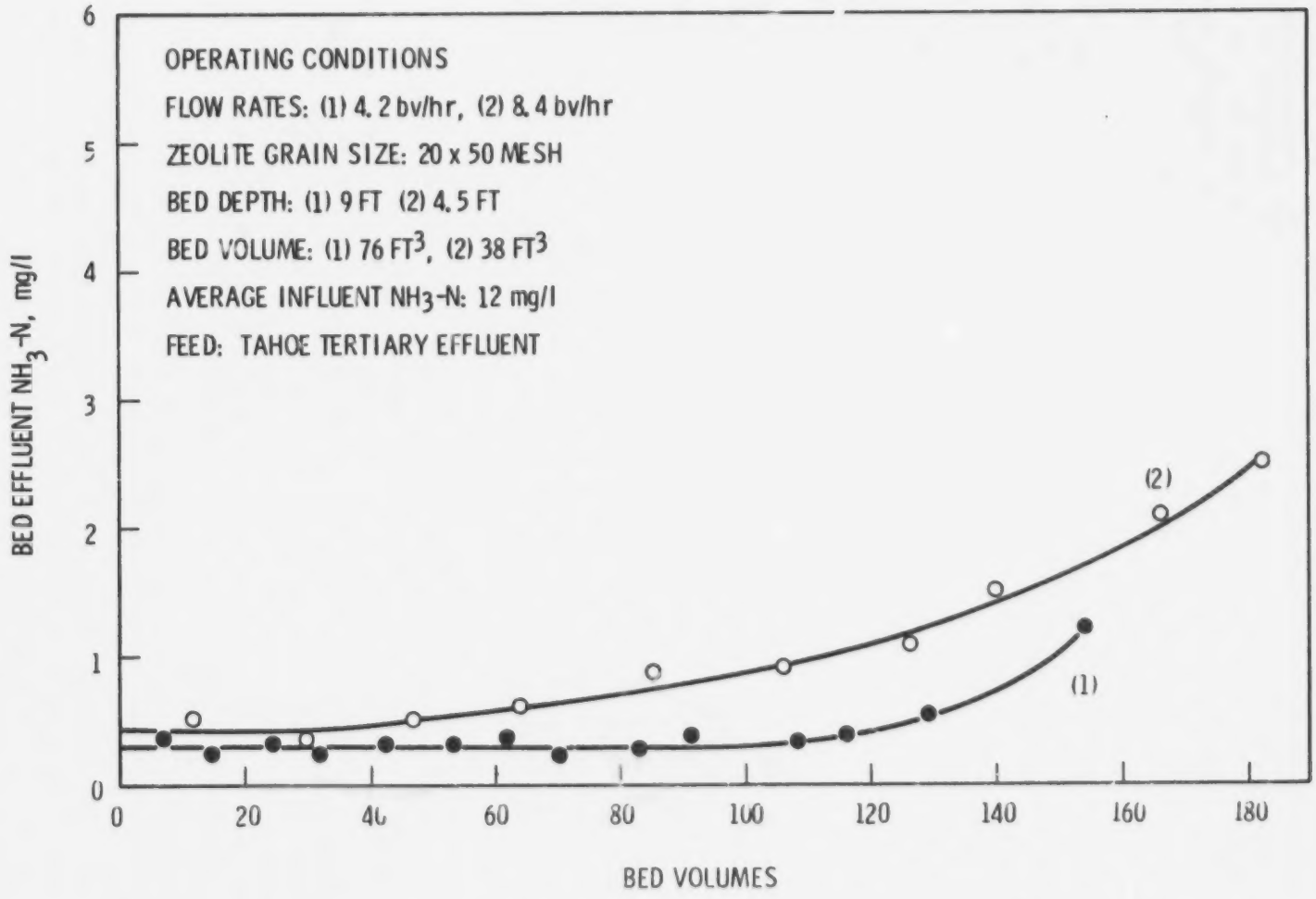

FIGURE 7. EFFECT OF BED DEPTH ON AMMONIA BREAKTHROUGH AT 4.8 gpm/ft^2 FLOW RATE

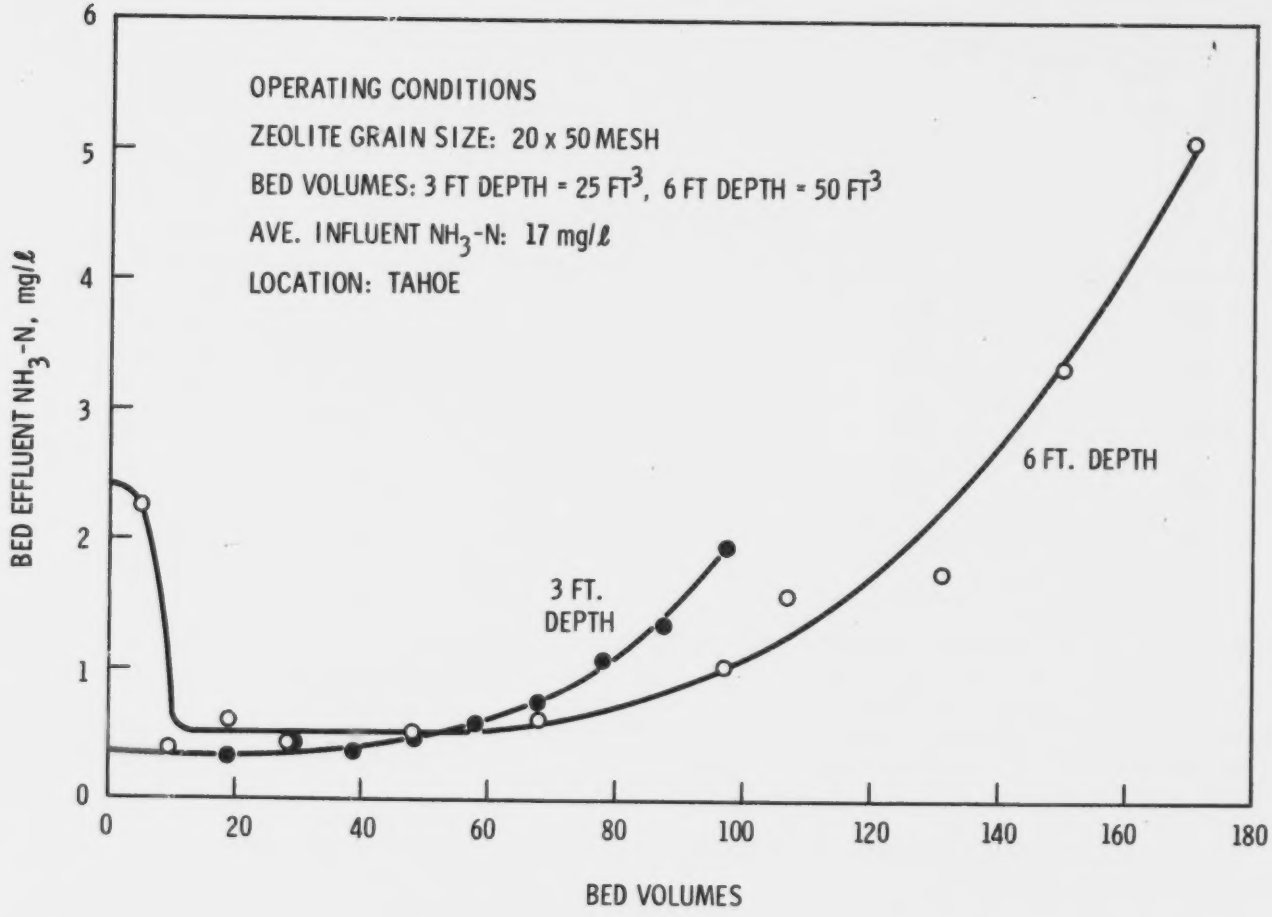

FIGURE 8. EFFECT OF BED DEPTH ON AMMONIA BREAKTHROUGH AT 9.7 bv/hr

TABLE 2

TAHOE PERFORMANCE DATA FOR SIX RUNS WITH TWO COLUMNS IN SERIES

Run No.	Loaded Column	Ave. Conc. of NH_3-N in Product mg/liter	Ave. Conc. of NH_3-N in Influent mg/liter	Column Vols. Through Loaded Column to 1.0 mg/l Effluent Breakthrough	Percent of NH_3-N Capacity Used
1	A	0.325	11.8	290	91
2	C	0.42	15.6	168	62
3	B	0.38	10.3	311	90
4	A	0.43	15.0	229	83
5	C	0.66	16.1	215	81
6	B	0.44	13.3	306	102

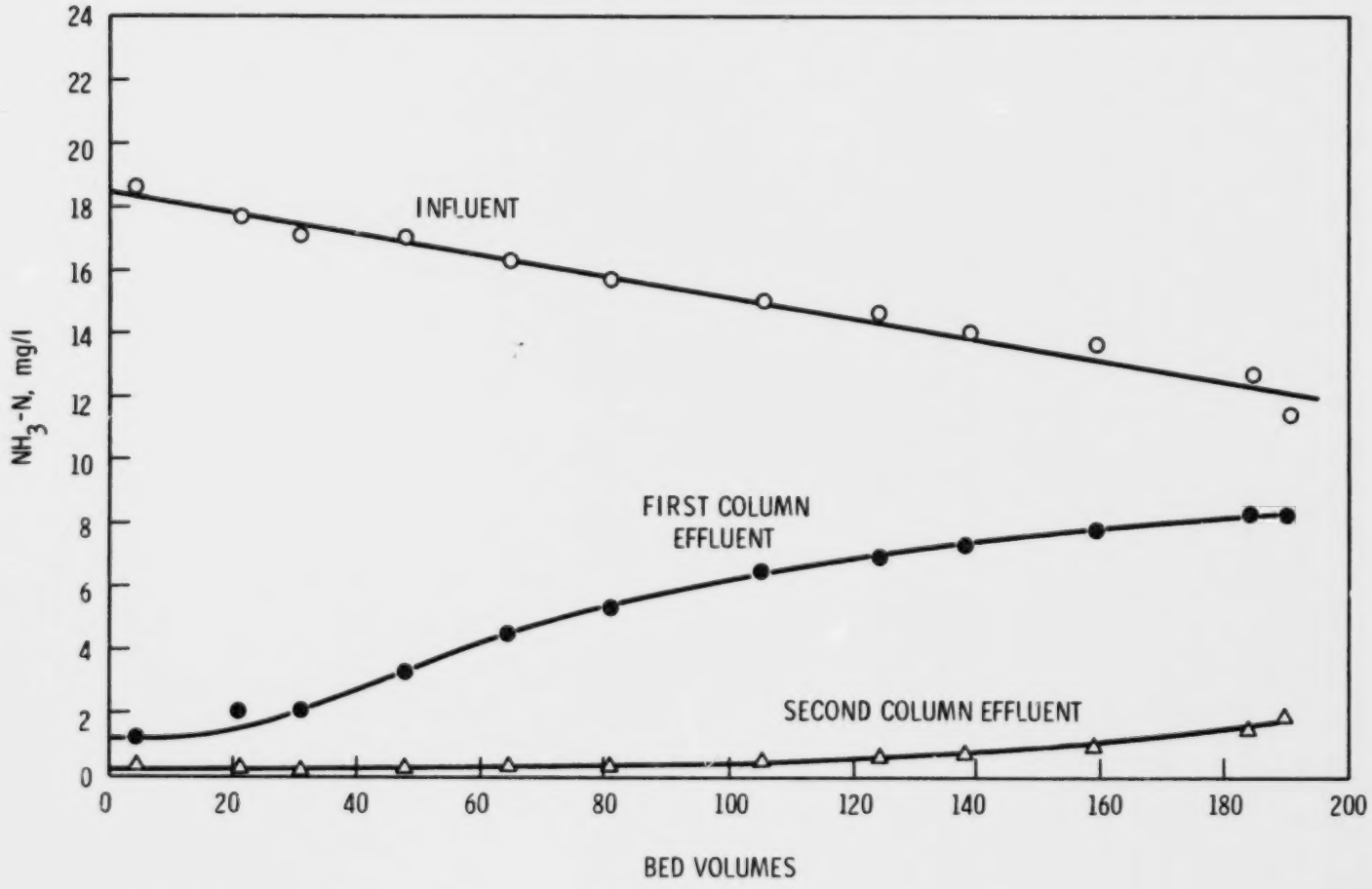

FIGURE 9. AMMONIA BREAKTHROUGH CURVES FOR 1ST AND 2ND COLUMNS IN SERIES WITH TAHOE TERTIARY EFFLUENT

Performance data for 17 semi-countercurrent runs at Blue Plains with two columns in series are listed in Table 3. The average bed volumes processed per run was 232 and the average NH_3-N in the influent and effluent was 12 mg/l and 1.4 mg/l, respectively. An incomplete regeneration and high feed pH in two cases caused a significant increase in the average effluent NH_3-N concentration. Excluding runs 1, 5, 12, and 14, the average NH_3-N concentration is 0.93 mg/l for an average removal 93%. The average bed volumes processed at Blue Plains was about 67% of the total available capacity, which is less than that experienced at Tahoe. It is believed that the relatively high organic concentration in the clarified raw sewage feed stream at Blue Plains was responsible in part at least. The differential pressure increased across the zeolite beds during operations at Blue Plains as a result of biological growth in the beds. The growth was effectively removed during regeneration and backwashing.

The latter runs made at each site should have been closer to steady-state. However, there did not appear to be any definite trend in breakthrough throughputs for specific columns at Tahoe or Blue Plains. It appears that all semi-countercurrent loading runs were essentially at steady-state.

Zeolite Attrition

Accurate zeolite volume measurements were made at Tahoe in "A" column only since no screen leaks developed in the column with resultant loss of zeolite. The total zeolite volume reduction in "A" column through 15 cycles was 2.6% or 0.17% per cycle. The average ion exchange capacity of the zeolite in all columns at the start of operations was 1.64 milli-equivalents per gram. The average ion exchange capacity at the termination of 15 runs per column was 1.63 milli-equivalents per gram.

TABLE 3

PERFORMANCE DATA FOR SEVENTEEN RUNS AT
BLUE PLAINS WITH TWO COLUMNS IN SERIES

	Ave. Flow Rate (gpm)	Ave. Conc. of NH_3-N in Influent (mg/l)	Ave. Conc. of NH_3-N in 1st Col. Eff. (mg/l)	Ave. NH_3-N Conc. of Product (mg/l)	Bed Volumes Treated By Loaded Column	Percent of NH_3-N Capacity Used
1 (a)	30	10.0	2.4	0.61	270	68
2	36	14.0	4.6	0.78	355	109
3	40	11.0	6.0	0.76	298	79
4	40	12.3	6.9	0.62	154	44
5 (b)	40	11.6	3.2	7.0	154	43
6	31	12.5	6.8	0.53	174	56
7	30	12.2	5.8	0.53	203	68
8	30	11.5	1.9	0.38	154	47
9	50	11.4	4.7	1.13	310	95
10	50	10.6	5.9	1.39	265	69
11	40	11.8	4.6	0.96	152	42
12 (c)	40	10.3	4.6	2.37	210	54
13	40	11.7	5.6	1.19	238	66
14 (c)	50	13.6	3.0	2.29	262	79
15	50	13.3	5.9	1.18	215	64
16	50	13.4	5.9	0.98	300	90
17	50	12.7	6.0	0.84	237	69

(a) two freshly regenerated beds in series
(b) second column was not completely regenerated
(c) feed pH was 10 for 1-2 hours

REGENERATION STUDIES

Normal Pilot Plant Regeneration

Normal regeneration during the pilot plant studies utilized a mixture of NaCl and $CaCl_2$ in a solution adjusted to a pH of about 11 using lime. The total salt concentration was generally equivalent to 0.1 N NaCl which will equilibrate to a 0.02 N NaCl, 0.08N $CaCl_2$ solution upon continued reuse with lime addition. During regeneration the regenerant was continuously recirculated through the zeolite bed and air stripping column with lime addition before return to the bed. Sodium chloride is added to the regenerant because significant amounts of sodium ion have been found to give longer service cycles and more rapid elutions (see Figure 5 of Appendix C). Make-up salt is added as needed to replace that lost due to incomplete removal of regenerant following the regeneration cycle. High pH favors NH_3 production necessary for air stripping. A higher salt solution (total normality about 2) was subsequently chosen to assure effective ammonia elution by a batch recycle regeneration method using 4 bed volumes of regenerant at pH 11. Computations based on equilibrium data indicate that ammonia elution is increased from 60% to 88% by increasing the salt concentration of 4 bed volumes of regenerant from 0.1 N to 2.2 N at pH 11. Further increases in the salt concentration, in particular the Ca^{+2} concentration, will reduce the maximum pH that can be attained by lime addition to values significantly less than 11.

The problems due to the precipitated solids formed during regeneration with lime solutions were quite severe at Pomona when employing normal continuous regenerant recycle. The magnesium content of the Pomona feed stream was approximately 20 times that of Tahoe. Examination of a zeolite bed after regeneration at Pomona disclosed the presence of large chunks of white material which was largely composed of magnesium hydroxide. This material apparently filtered out on the retaining screens at the top of the zeolite columns and periodically fell back into the bed when flow reversals were used to reduce the pressure across the bed. A photograph of the chunks of white material on top of a bed of clinoptilolite is shown in Figure 10.

Both high rate backwashing with tap water and treatment with dilute acid were temporarily effective in restoring good performance with the zeolite beds, as illustrated in Figures 11 and 12. However, the use of acid is expensive both with respect to the cost of the acid used and the cost of the acid resistant piping and vessels required. High rate backwashing was continued for each run after that for Curve 2 in Figure 11, but was not consistent in restoring good performance. The basic problem occurred during regeneration where a thorough elution was not always obtained due to particulate matter blocking off portions of the bed. Removal of the particulate matter was deemed necessary for satisfactory performance. The effect of clarifying the regenerant before recycling through the zeolite bed is illustrated in Figure 13. Clarification was accomplished with the slightly inclined tube settlers in the filtration unit.

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FIGURE 10. PHOTOGRAPH OF WHITE MATERIAL ON TOP OF A BED OF CLINOPTILOLITE AT POMONA

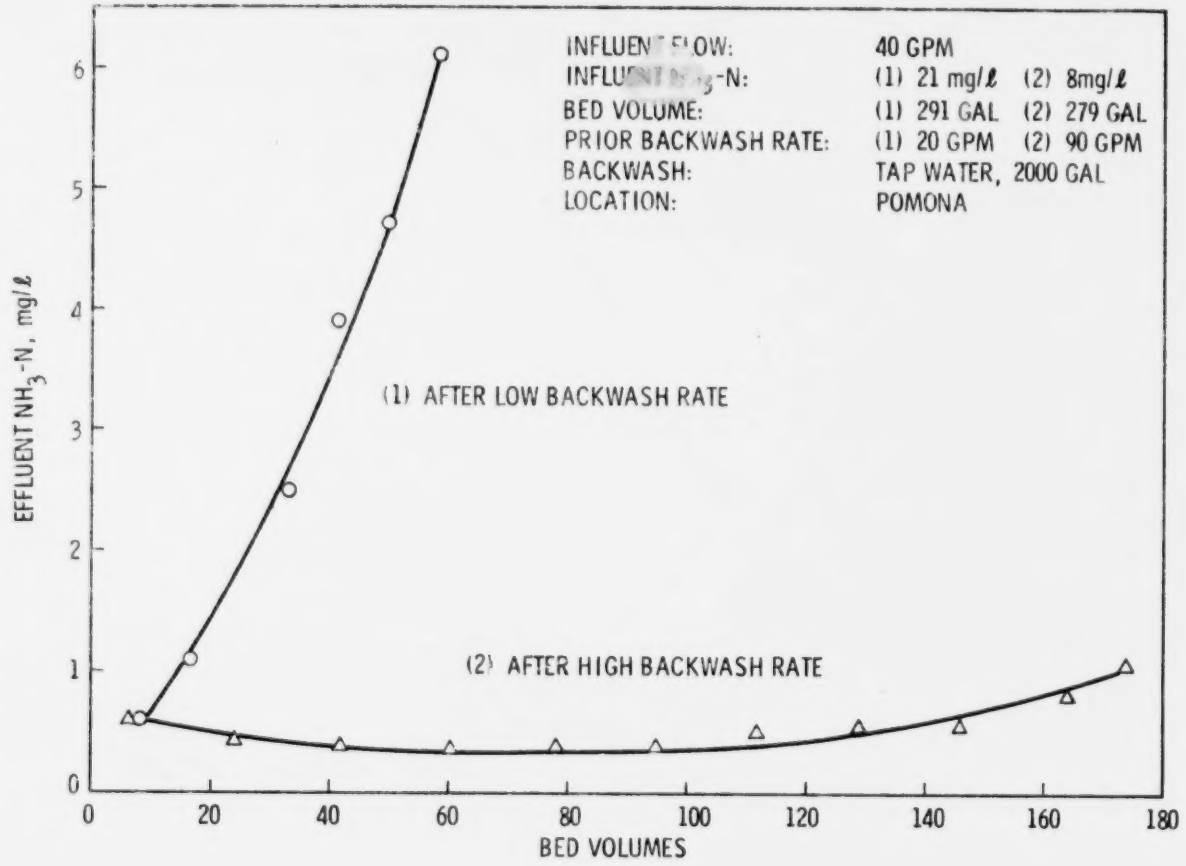

FIGURE 11. EFFECT OF PURE WATER BACKWASH RATE ON SUBSEQUENT NH_3-N BREAKTHROUGH

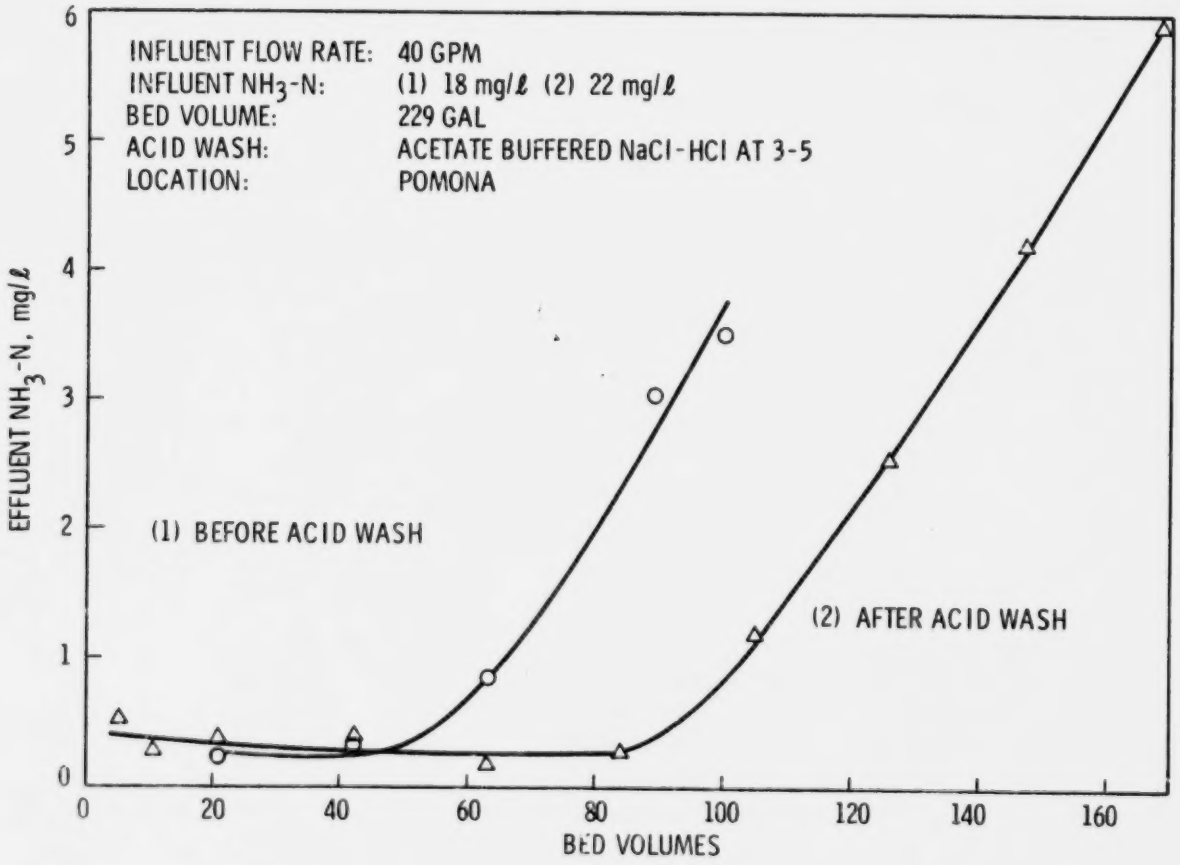

FIGURE 12. EFFECT OF ACID WASH ON SUBSEQUENT NH_3-N BREAKTHROUGH

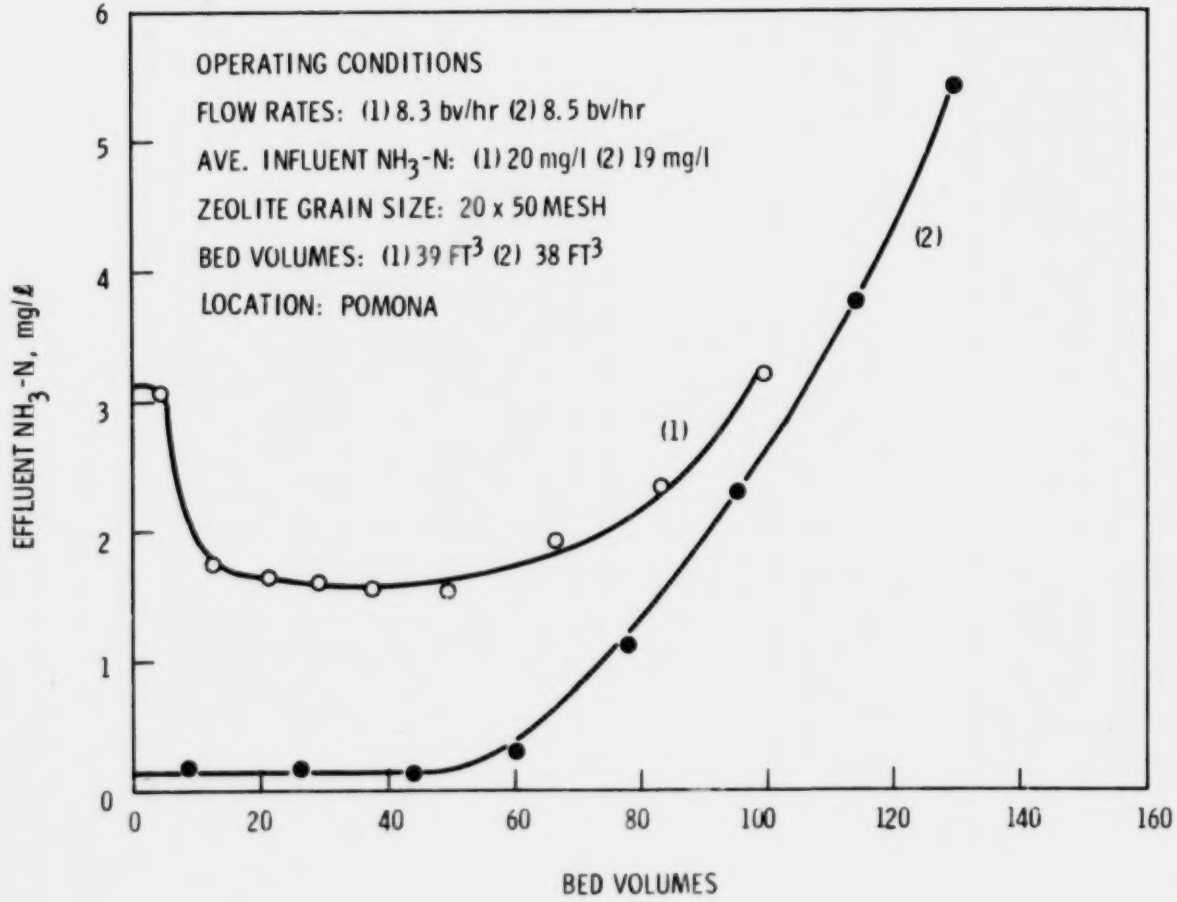

FIGURE 13. AMMONIA BREAKTHROUGH CURVES FOR COLUMNS FOLLOWING REGENERATION WITH UNCLARIFIED (1) AND CLARIFIED (2) REGENERANT WITH HIGH MAGNESIUM CONTENT

Figure 13 shows significant improvement in regenerant performance after clarification. The combination of high rate water backwashing with regenerant clarification should provide satisfactory regenerant solids removal with high magnesium operations.

Pilot Plant Batch Recycle Regeneration

In order to minimize the volume of regenerant required to elute the NH_3-N from the zeolite beds, a batch regeneration technique was studied at Tahoe. Normal regenerant was recycled through the bed only, deferring the air stripping operation. This was done to minimize the liquid volume to be stripped. Less liquid volume means less heat input required to prevent freezing and keep efficiency high during cold weather stripping operation.

Contact with several recycle batches may be necessary, however, to obtain good regeneration. A two batch recycle regeneration could proceed as follows. In order to start the regeneration scheme, a first batch of fresh regenerant could be recycled through a bed followed by a second batch of fresh regenerant recycled through the same bed. After this, the second batch recycle used for one bed could be used for the first batch recycle for the next bed. Each second batch recycle would consist of fresh or renovated regenerant. Pilot plant data were collected in order to set process specifications on a two batch recycle regeneration scheme.

Single batch recycle data show that the NH_3-N concentration in recycled regenerant increases rapidly from near zero to about 500 mg/l in a few hours with a zeolite bed loaded with an average of 2.24 g of NH_3-N per liter of bed. This loading is equivalent to ammonia removed during reduction of a 15 mg/l NH_3-N influent to a 1 mg/l (average) effluent using a 160 bed volume throughput. Three elution curves are illustrated in Figure 14 for this average bed loading using regenerant with a total salt concentration of 0.1 N. Curve 1 shows the lowest NH_3-N (450 mg/l) concentration after 6 hours, which is believed to be the result of the low pH (10.8). The NH_4^+ concentration at 450 mg/l NH_3-N and pH 10.8 is 8.9×10^{-4}M compared with 4.0×10^{-4}M NH_4^+ at pH 11.2 and 500 mg/l NH_3-N, and 2.1×10^{-4}M NH_4^+ at pH 11.5 and 520 mg/l NH_3-N. The amount of ammonia removed from the zeolite will, therefore, increase with pH (low solution NH_4^+ concentrations show low NH_4^+ zeolite adsorption). Curve 2 shows a slower rate of NH_3-N elution than Curve 3, which is believed due to a combination of the slower flow rate and lower temperature and pH. Curve 3 shows that equilibrium was approached after 4.5 hours. Curves 1 and 3 represent the recycle of 2.2 bed volumes, whereas Curve 2 represents 1.2 bed volumes.

Figure 15 illustrates a first and second batch recycle for a highly loaded zeolite bed (3.2 g/liter of bed) using regenerant with a total salt concentration of 0.1 N. The first batch was air stripped to 107 mg/l NH_3-N while recycling through both the zeolite bed and the stripping column. Regeneration was 75% complete at this point. The NH_3-N increased by 150 mg/l in the regenerant after 2 hours in the second batch recycle.

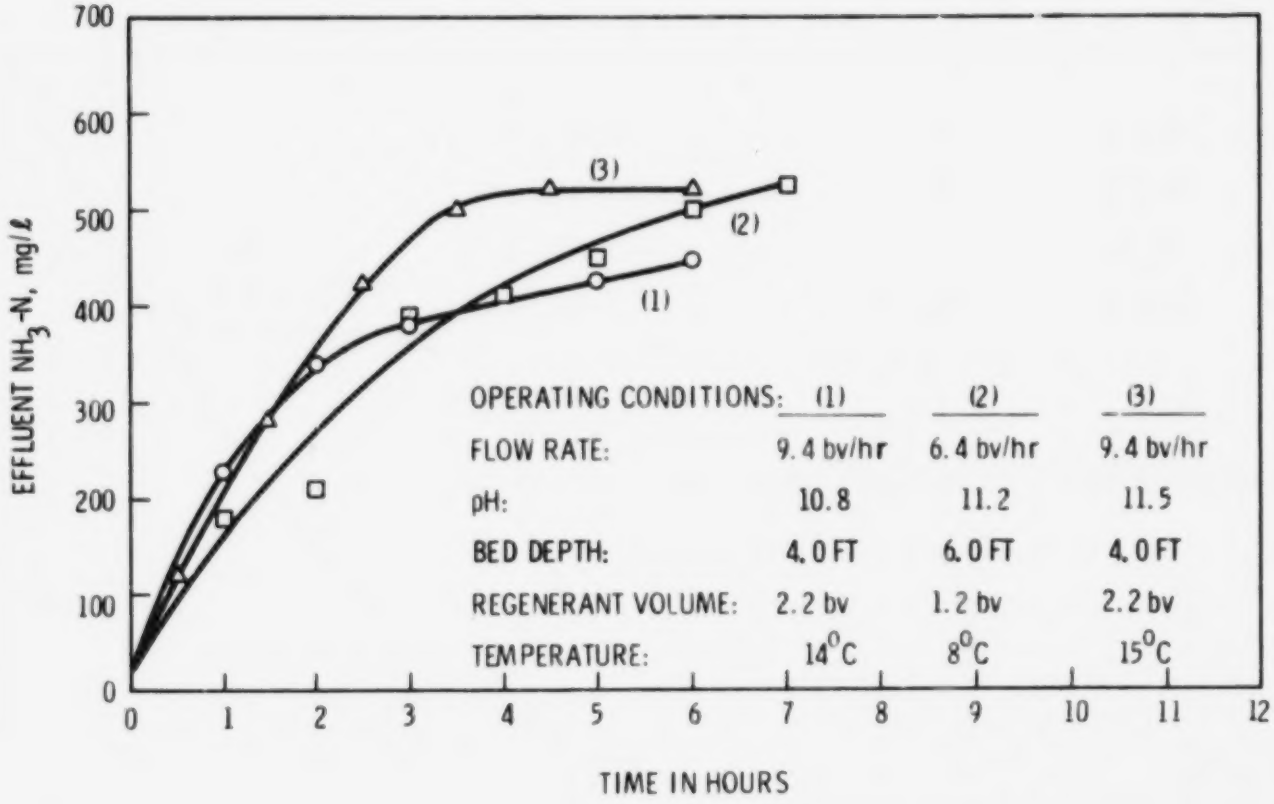
EFFLUENT NH_3-N, mg/ℓ
TIME IN HOURS
(1)
(2)
(3)
OPERATING CONDITIONS: (1) (2) (3)
FLOW RATE: 9.4 bv/hr 6.4 bv/hr 9.4 bv/hr
pH: 10.8 11.2 11.5
BED DEPTH: 4.0 FT 6.0 FT 4.0 FT
REGENERANT VOLUME: 2.2 bv 1.2 bv 2.2 bv
TEMPERATURE: 14°C 8°C 15°C

FIGURE 14. FIRST BATCH RECYCLE ELUTION CURVES

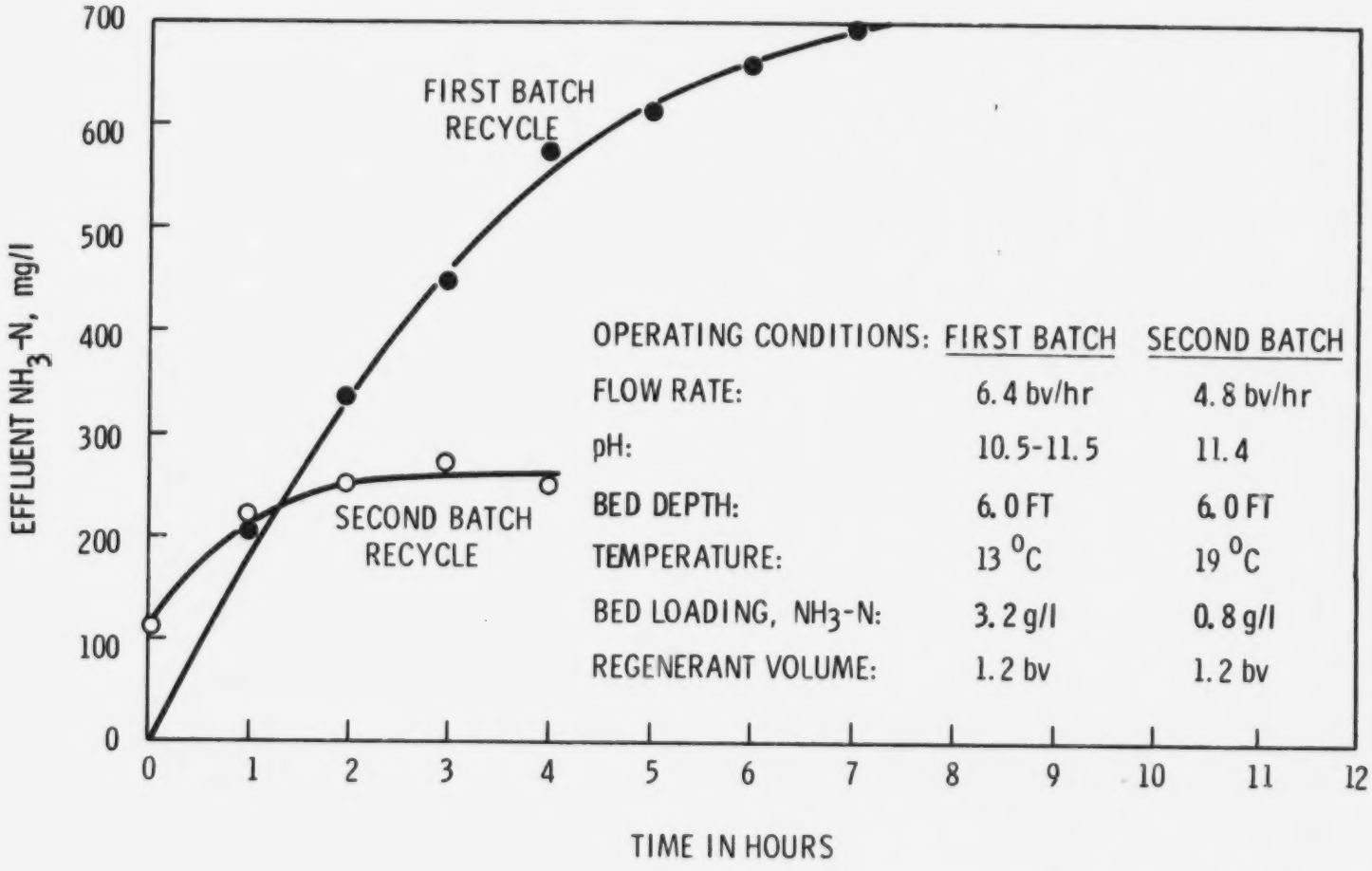

FIGURE 15. FIRST AND SECOND BATCH RECYCLE ELUTION CURVES

The time required for the second batch recycle (2 hours) was less than that of the first batch (4-6 hours) due to: 1) the time lag in reaching the optimum pH at the beginning of the first batch recycle; and 2) the lower temperature of the first batch recycle (9°C vs. 19°C).

The regenerant system was temporarily altered at Blue Plains to permit the recycle of 3.6 bed volumes of regenerant (1M $CaCl_2$ and 0.2M NaCl at pH 11). The results of this regenerant batch recycle are shown in Figure 16. The first recycle removed 75.4% of the ammonia from the zeolite bed and the second recycle removed 12.8% with the remainder accounted for by loss of ammonia during a flush between the two recycles. The flush consisted of air stripped first cycle regenerant which was pumped through the bed to remove regenerant that could not be drained after the first recycle. Essentially no regenerant could be drained from the column since the regenerant storage vessel was on the same level with the ion exchange vessel. The flush was air stripped to reduce the NH_3-N concentration to 10 mg/l.

In addition to collecting elution data, theoretical calculations were made. Equilibrium data were used to compute the maximum ammonia elution from clinoptilolite as a function of regenerant volume and pH. The results are given in Figure 17 for a pH range of 7 to 11 using an equilibrium regenerant solution at ratios of 2, 4 and 6 bed volumes of regenerant to 1 bed volume of clinoptilolite. The initial ammonia nitrogen loading on the clinoptilolite was 0.12 equivalents per liter or 1.7 grams per liter. The data in Figure 17 illustrates the importance of pH in removing sorbed ammonia during regeneration. The maximum elution values at pH 11 are higher than that shown for the first pilot plant recycle in Figure 16, which is believed to be the result of: (1) not including potassium salt in the recycled regenerant of the pilot plant run (potassium would build up naturally in extended recycle service), and (2) not attaining full equilibrium even though the pilot plant elution data indicates that a plateau was reached.

By examining the pilot plant data, a recommended regeneration scheme has been devised. For single column operation, a regenerant of 0.2 M NaCl, 1 M $CaCl_2$ and adjustment to pH 11.5 with lime is recommended for two batch recycle operation. Bed loadings will be lower in practice than used for the pilot plant studies. It is suggested that 4 bed volume recycle batches be used at 10 bv/hr recycle rate with 2 hours for each recycle. This should permit a change in concentration in the first batch recycle regenerant from 100 to 600 mg/l NH_3-N (a change of 500 was experienced experimentally on a fresh batch) and in the second batch recycle regenerant from 10 (from regenerant renovation) to 100 mg/l NH_3-N with almost complete NH_3-N removal from the zeolite beds.

It should be emphasized that further practical experience may indicate changes in regeneration procedure specifications. Calcium and sodium concentrations were fixed rather arbitrarily in the experimental studies

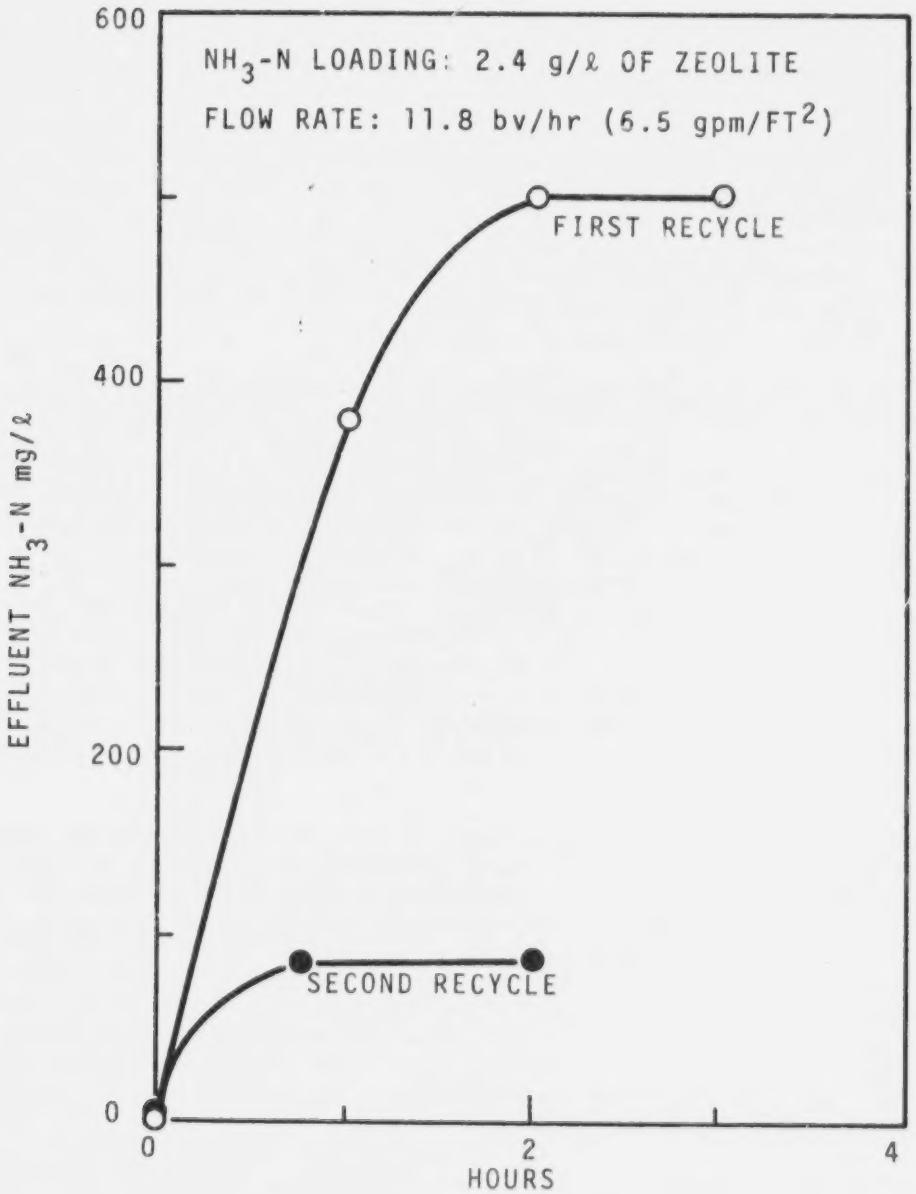

FIGURE 16. REGENERANT BATCH RECYCLE WITH 3.6 BED VOLUMES OF 1 M $CaCl_2$-0.2 M NaCl AT pH 11

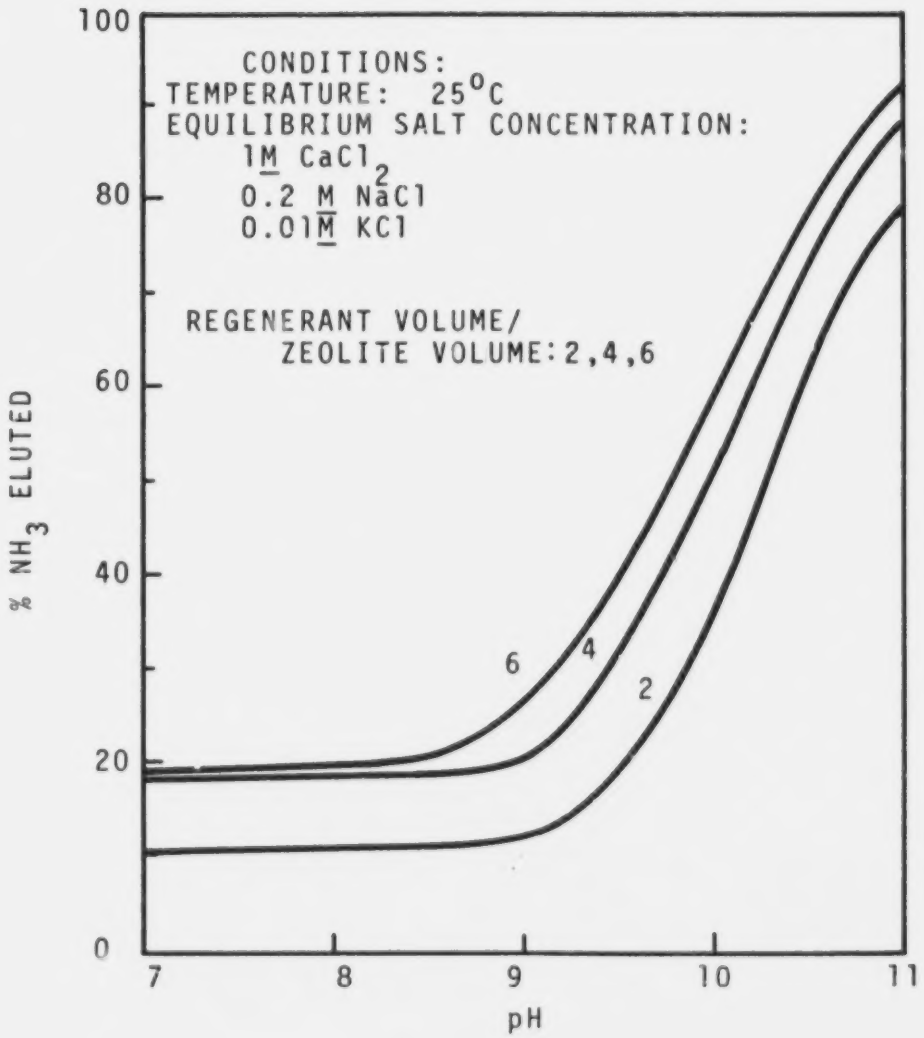

FIGURE 17. EFFECT OF REGENERANT VOLUME AND pH ON AMMONIA ELUTION

and the regeneration procedure recommended above, although thought to be realistic and adequate, may not be optimal. Also, the concentration suggested for the regenerant need not be fixed at start-up. The process could be started with 2 N NaCl, for example, and adjusted during operation. This was actually done during the pilot study on electrochemical renovation to be discussed later.

REGENERANT RECOVERY

Air Stripping of Regenerant

The spent regenerant containing ammonia was recovered for reuse by air stripping in a 3.6 ft. diameter by 8 ft. column packed with 1 inch polypropylene Intalox(R) saddles. The regenerant was normally recycled upflow through the zeolite bed at a flow rate of 4.8-7.1 gpm/ft^2 until the NH_3-N approached a maximum concentration. The regenerant was then recycled through both the zeolite bed and the air stripper until the NH_3-N was reduced to about 10 mg/1. The liquid flow rate to the stripper was normally 20 gpm with an air/liquid ratio of 150 cfm/gpm. Ammonia removal in the air stripper generally averaged about 40% at 25°C. Calcium carbonate scaling occurred on the polypropylene saddles, but did not interfere with stripping efficiency for operating periods up to 65 days at each site. The calcium carbonate scale formed during the Tahoe and Pomona operations was flaky and could be removed to a large degree by spraying with water. The scale formed during operations at Blue Plains was relatively hard and required water fluidization of the packing to remove the scale.

The type of air stripper used in the mobile pilot plant is not recommended for general plant use because of the energy wasted in blowing air through the packing. A modified cooling tower with low differential pressure across the tower is recommended.

Electrochemical Renovation of Regenerant

The chemical destruction of ammonia in regenerant solutions from the selective ion exchange process was investigated as an alternative method to air stripping, since atmospheric disposal of ammonia may be undesirable in some locations. The chemical destruction of the ammonia is accomplished by reaction with chlorine, which is generated electrolytically in the regenerant solution. This process can be carried out under neutral conditions and is not as prone to solids precipitation as alkaline lime regeneration. Regenerant solutions from the selective ion exchange process are rich in NaCl and $CaCl_2$ (plus $MgCl_2$ when Mg^{+2} is present in the feed stream to the clinoptilolite beds). These salts provide the chlorine that is produced at the anode of the electrolysis cell.

The chemical reactions that take place in the electrolysis cell are illustrated below using NaCl as an example:

Cathode: $Na^+ + e^- = Na$ (1)

$2Na + H_2O = 2NaOH + H_2\uparrow$ (2)

Anode: $2\ Cl^- - 2e^- = Cl_2$ (3)

$3Cl_2 + 2\ NH_4Cl = N_2 + 8HCl$ (4)

The overall reaction for the destruction of ammonia with chlorine is shown above. Excess dissolved Cl_2 exists as hypochlorite (HOCl). The hydrochloric acid produced by reaction (4) is partially neutralized by the NaOH produced by reaction (2). However, an excess of hydrochloric acid is produced and base must be added to the system to maintain a neutral solution. The moles of base added should be equivalent to the moles of NH_4Cl to be reacted. The production of acid, in fact, is a good indicator that the reactions are taking place, and the break point is clearly indicated by stabilization of the pH.

A laboratory model electrolysis cell was obtained for conducting laboratory experiments. The anode, which is the most vulnerable part of the cell, is composed of a 5/16 inch diameter graphite rod coated with lead dioxide. The lead dioxide coating is very resistant to attack by chlorine or oxychloro-acids. Commercial anodes made of this material are used in the production of chlorate and perchlorate. It is of interest to note that ammonia impurity in the brine is destroyed early in the production of sodium chlorate by electrolysis of brine.

Initial laboratory results with the electrolysis cell show that 5 g of NH_3-N was essentially destroyed in two hours and forty-five minutes with the cell operating at 10 amps and 5.5 to 9 volts. A simulated regenerant solution (1.87 N $CaCl_2$, 1.31 N $MgCl_2$, 0.14 N NaCl and 0.01 N KCl) containing the ammonia as NH_4Cl was recirculated through the cell at flow rates of 500 to 1000 ml/min. The cell has 10 in^2 of anode surface area. At an average of 7.3 volts and 10 amps, the electrical energy required to destroy one gram of NH_3-N is 40 watt hours. When related to the treatment of 1000 gallons of wastewater containing 15 mg/l NH_3-N (total 57 g), the energy consumption would be 2.3 KW hours.

Although major solids precipitation was avoided, a white material was formed on the cathode during the above experiment. Some of this material was washed off the cathode and collected in the regenerant container. Subsequent analysis revealed this material to be a mixture of $Ca(OH)_2$ and $Mg(OH)_2$. The increase in cell resistance, which required an increase from 5.5 volts to 9 volts in order to maintain a current of 10 amps, was due to this coating of mixed $Ca(OH)_2$ and $Mg(OH)_2$ on the cathode. Calcium and magnesium are plated on the cathode where they react with water to form their respective hydroxies. Due to the low solubility of these hydroxides, they tend to precipitate and collect on the surface of the cathode. Subsequent experiments with and without $MgCl_2$ in the simulated regenerant solutions indicate that the $Mg(OH)_2$ increases the conductivity of the coating but reduces its solubility in acid. The effect of Mg^{+2} on the resistance of the cell is illustrated in the attached Figure 18.

Turbulent flow promoted by baffling or other cell modifications is expected to minimize the scale formation rate. The effects of pH and flow rate on the cell resistance were found to be insignificant. The data obtained at pH's of 4 and 5 and flow rates of 4 and 15 1/min are shown in Figure 19.

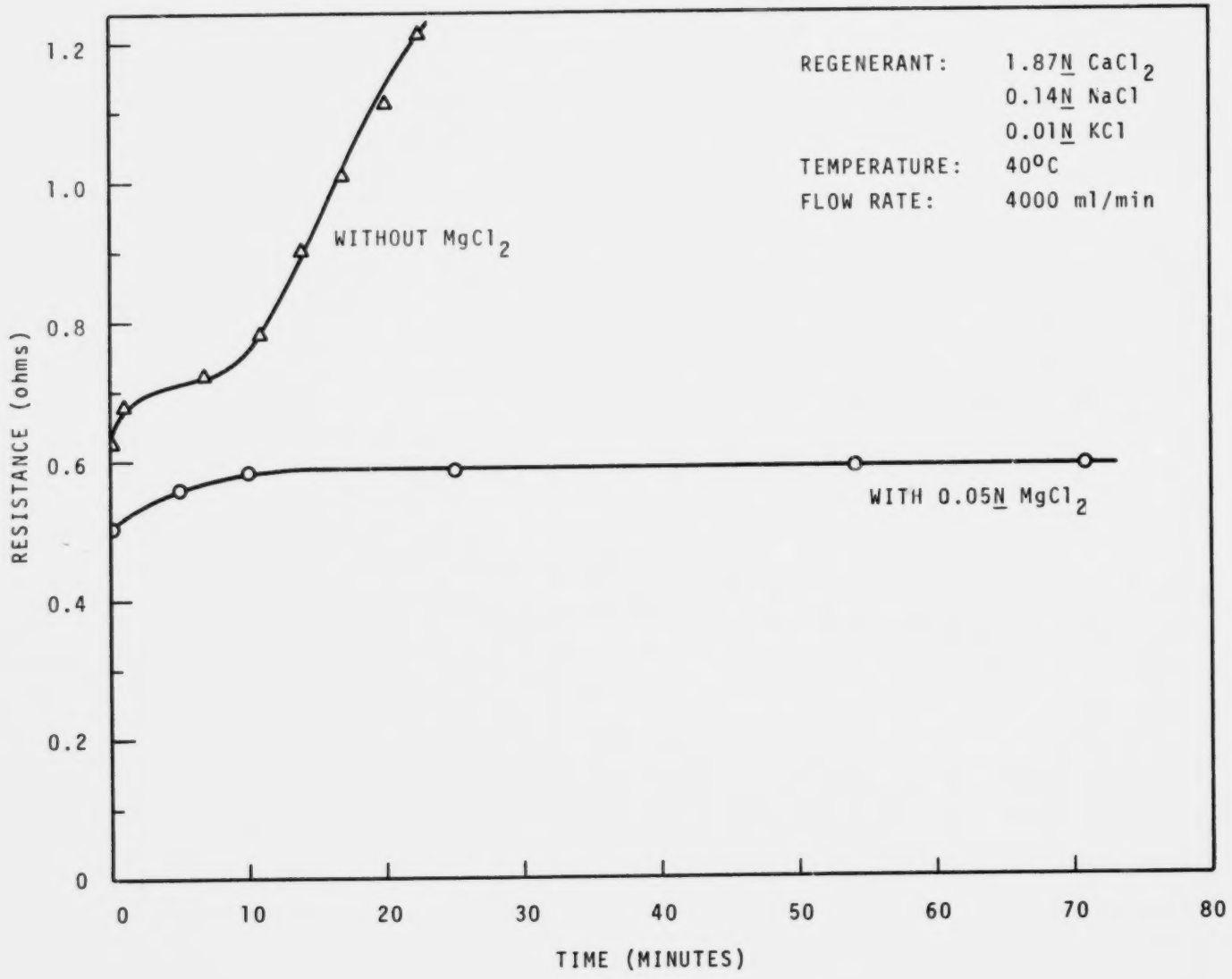

FIGURE 18. EFFECT OF Mg^{+2} ON CELL RESISTANCE

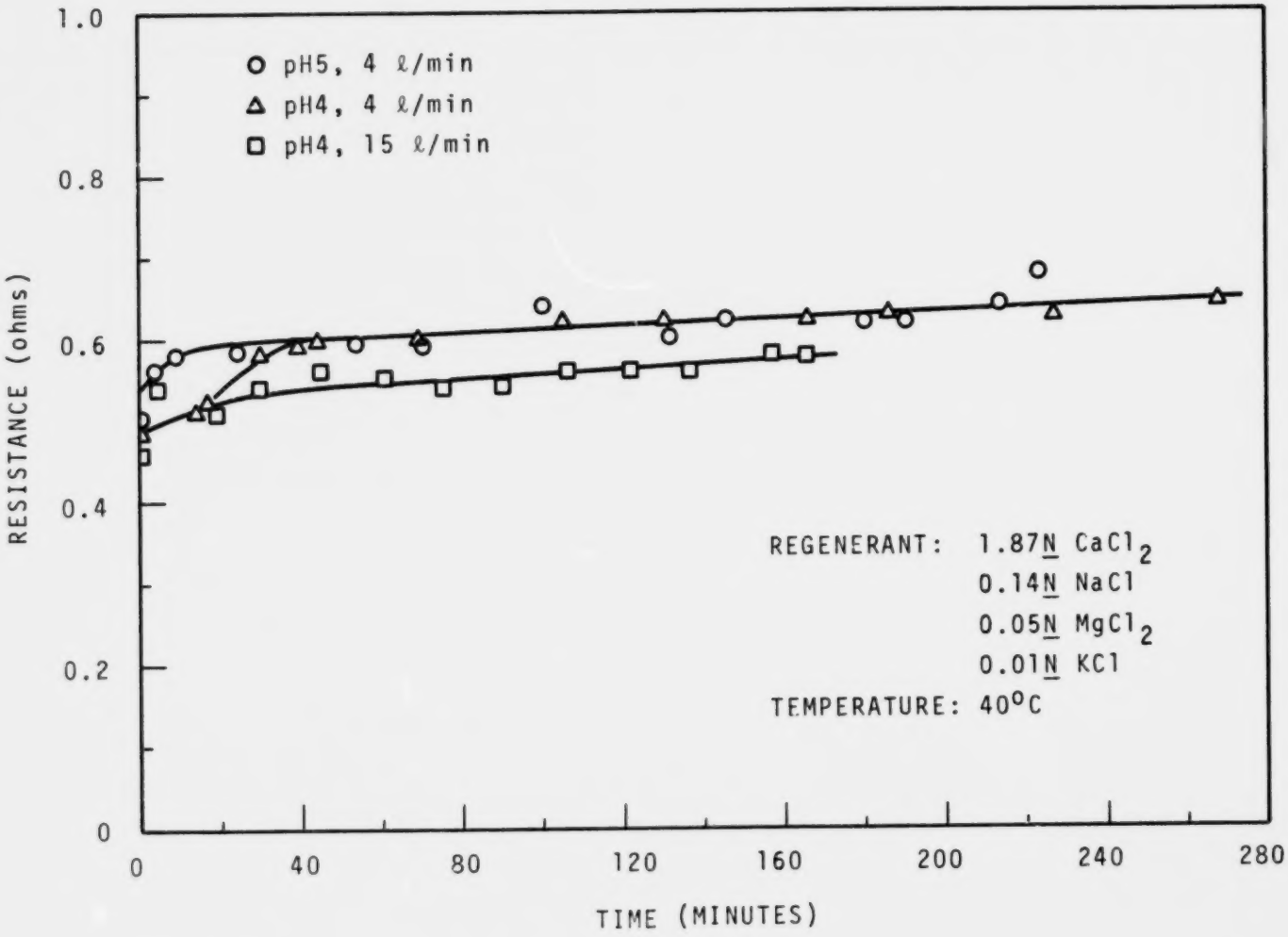

FIGURE 19. EFFECT OF H^+ ACTIVITY AND FLOW RATE ON CELL RESISTANCE

Preliminary pilot scale studies were conducted at the Blue Plains plant to further evaluate electrochemical regenerant renovation. Two 500 amp electrolysis cells and a 2000 amp, 6 volt rectifier were installed near the mobile pilot plant for ammonia removal, along with a 20 HP pump and a 2500 gallon regenerant treatment tank (swimming pool). Brine (NaCl) was used as the regenerant in these pilot studies. Use of a 2 M NaCl brine was planned but some difficulty was encountered as discussed below and the actual concentration was 0.9 M NaCl. Regeneration of the clinoptilolite beds in the mobile pilot plant was accomplished by pumping brine from the regenerant storage tank (in the Recla-Mate SWB treatment unit in the trailer) upflow through the zeolite beds to the regenerant treatment tank. When all of the brine was collected in the regenerant treatment tank, recirculation of the brine through the electrolysis cells was started. Based on laboratory data, the two 500 amp cells are capable of destroying about 150 grams of ammonia nitrogen per hour in chemically pure solutions. Chlorine is produced at the surface of the lead dioxide anode in the cells where it reacts with the solution to produce hypochlorite. Chlorine is produced at the rate of 657 g per hour when the total current applied to the cells is 1000 amps.

Since both the Recla-Mate SWB unit and the regenerant treatment tank each holds only half of the required volume of regenerant, it was necessary to put the regenerant through each bed twice. Data on elution with neutral regenerant is included in Appendix B. Ammonia destruction was accomplished after each transfer except for the second batch of the final run. Ammonia elution from the clinoptilolite beds did not appear to be as rapid as that expected for a 2 M solution. Although sufficient salt (2000 lbs NaCl) was added to the SWB unit to make a 2 M NaCl solution, subsequent analysis of the regenerant showed that it contained only 0.9 moles per liter. It is believed that some concentrated brine was lost through the filter of the SWB unit during the dissolution step. Since the conductivity of the solution in the electrolysis cells was satisfactory, no significant loss was suspected at the time.

Three zeolite beds were regenerated with the brine; however, only two of the beds were loaded with ammonia. The first bed was assumed to be partially loaded after regeneration with a lime-salt solution, but was subsequently found to contain very little ammonia as evidenced by the low NH_3-N concentrations in the brine during the first run.

The highest NH_3-N levels were attained in the first batches of brine from the second and third runs and were 248 mg/l and 210 mg/l for 1800 gal and 2100 gal, respectively. The difference in regenerant volumes was due to incomplete draining of the column during the second run. Gassing in the zeolite bed caused by release of nitrogen from the destruction of ammonia was suspected as the cause of the incomplete draining, since a significant amount of hypochlorite was present in the brine after the first run. Gassing was also observed in the laboratory when a clinoptilolite bed was eluted with brine containing a relatively high concentration of hypochlorite. The electrical energy consumed by the first batches from the second and third runs was 5.67×10^7 coulombs and 4.60×10^7 coulombs,

respectively. The amount of energy per gram of NH_3-N was 33,600 coulombs and 27,500 coulombs with a power consumption of 54 and 46 watt hours/g, respectively. The energy and power consumed in the second batch of brine in the second run was 22,000 coulombs and 35 watt hours per gram, respectively. The second batch contained 72 mg/l NH_3-N. The electrolysis cells were operated at 1000 amps and 5.8 to 6.0 volts for the most part. No significant increase in cell resistance was noted, but the differential pressure across the cells increased with time as a result of scale formation. The difference in electrical energy consumption may be due to a difference in the amount of organic matter in the regenerant, although this has not been determined yet. The zeolite beds were given a short backwash to remove slime from the bed prior to regeneration and some variation in the amount of this material remaining after backwash may have existed between the two runs. Clarified raw sewage was used to load the zeolite beds at Blue Plains and this may have caused the slime. The slime problem will not be significant if the zeolite columns are operated after carbon columns which sorb the organic nutrients causing the slime.

Breakpoint chlorination for the first batch of regenerant in Run 3 is illustrated in Figure 20. The total NH_3-N remaining in the brine after 13 hours of treatment was 0.16 mg/l. The nitrate-nitrogen present in the brine was 8.0 mg/l. The latter represents the total produced by the two runs or a 1.7% conversion of NH_3-N to NO_3-N. No ammonia was detectable by direct nesslerization at the breakpoint of each batch. The Ca^{+2} increased from 1900 mg/l in 1800 gal after the second regeneration to 2700 mg/l in 2100 gal after the third regeneration. Lime was used to neutralize the acid formed by the destruction of NH_4Cl.

Ammonia leakage was relatively high after regeneration with the 0.9 M NaCl. The high leakage (1-3 mg/l NH_3-N) is attributed largely to high pH in the zeolite beds during the initial part of the service cycle. The high pH was apparently caused by residual lime left in the system by previous lime regenerations. The service cycle times were 37 hours and 34 hours (318 bed volumes and 292 bed volumes, respectively) on the two loaded columns regenerated with electrolytically renovated brine.

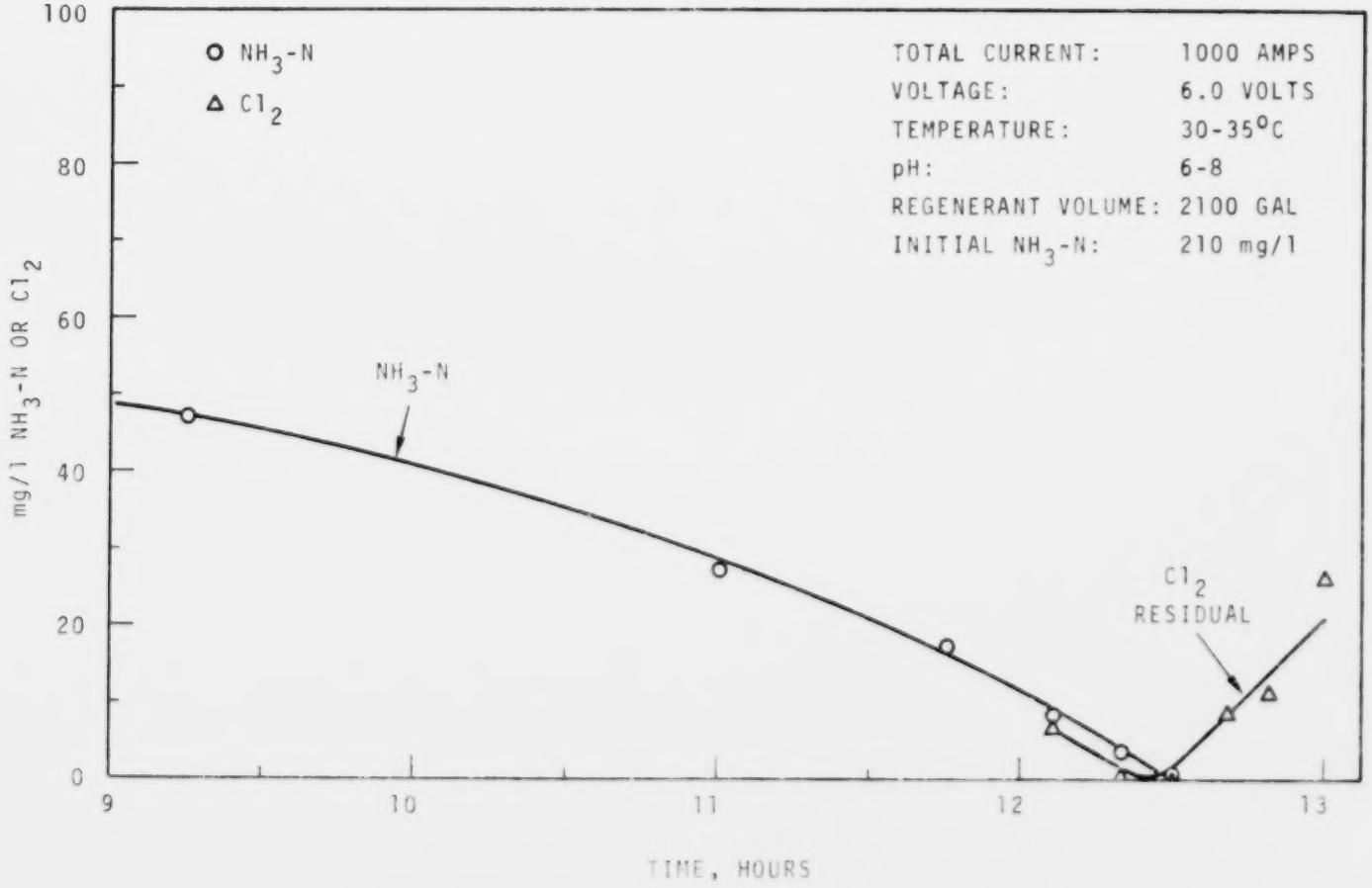

FIGURE 20. BREAKPOINT CHLORINATION OF REGENERANT BATCH #1, RUN 3

ACKNOWLEDGMENTS

The studies reported herein were conducted by personnel of the Pacific Northwest Laboratories, otherwise known as Battelle-Northwest, a division of Battelle Memorial Institute. Basil W. Mercer and Ronald C. Arnett served as Technical Director and Pilot Plant Engineer, respectively. The efforts and assistance of the following Battelle personnel contributed to the successful completion of the project. Pilot plant operations: Neil Bonney, James A. Coates, Marvin J. Mason, Richard G. Parkhurst, R. Gregory Swank and Robert G. Upchurch. Bench scale and theoretical studies: John G. Adams, David A. Cochran, Gaynor W. Dawson, and R. Jeff Serne. Technical and administrative assistance: Lloyd L. Ames, Gordon L. Culp, Douglas E. Olesen, Alan J. Shuckrow and C. Joseph Touhill.

Our sincere appreciation is extended to the following individuals outside Battelle whose cooperation and assistance made this work possible. Mr. Russell L. Culp of the South Tahoe Public Utility District, South Lake Tahoe, California; Mr. David R. Evans of Cornell, Howland, Hayes, and Merryfield, Engineers and Planners, Corvallis, Oregon; Messrs. Jerry C. Wilson and Harlan E. Moyer of Clair A. Hill and Associates, Consulting Engineers, Redding, California; Mr. Charles W. Carry of the Sanitation Districts of Los Angeles County, Los Angeles, California; Mr. John N. English of the Environmental Protection Agency, Water Quality Office, Pomona, California; Mr. Gerald Stern of the Environmental Protection Agency, Water Quality Office, Los Angeles, California; Mr. Dolloff F. Bishop of the Environmental Protection Agency, Water Quality Office, Washington, D. C.; and Mr. Alan Cassel of the District of Columbia Sanitation District, Washington, D. C.

The support of the project by the Environmental Protection Agency, Water Quality Office and the assistance and suggestions provided by Dr. Robert B. Dean, WQO Project Officer, are gratefully acknowledged. Also appreciated are the technical and editorial suggestions made by Dr. Harry Bostian of the Environmental Protection Agency during review of the report.

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APPENDIX A

SAMPLE CALCULATION OF AMMONIUM ION LOADING USING ACTIVITY COEFFICIENTS

The experimentally measured selectivity coefficient is defined as

$$K_A^B = \frac{(B)_s^b \, (A)_z^a}{(A)_s^a \, (B)_z^b} \qquad \text{(A-1)}$$

where

$(A)_s$, $(B)_s$ = normality of cations A and B in equilibrium solution

$(A)_z$, $(B)_z$ = equivalent fractions of cations A and B on the zeolite

a, b = the number of cations A and B represented in the chemical reaction for exchange of A and B.

A "thermodynamic"selectivity coefficient incorporating activity coefficients can also be defined:

$$K_{A\ \text{thermo}}^B = \left[\frac{\gamma_B^b \, (B)_s^b \, (A)_z^a}{\gamma_A^a \, (A)_s^a \, (B)_z^b}\right] \qquad \text{(A-2)}$$

The γ's are activity coefficients that correct for solution non-ideality and the "thermodynamic" selectivity coefficient is therefore a constant value for solutions having different concentrations of ions but the same ratio of A to B. It is assumed that corrections are not necessary for ions adsorbed on the zeolite. The invariance in the thermodynamic coefficient serves as the basis for a procedure to correct experimental values and calculate equilibrium zeolite loadings.

The experimental selectivity coefficients were determined in a reference solution of 0.1 N in cations. The thermodynamic selectivity coefficient can be expressed in terms of this reference solution:

$$K_{A\ \text{thermo}}^B = \left[\frac{\gamma_B^b \, (B)_s^b \, (A)_z^a}{\gamma_A^a \, (A)_s^a \, (B)_z^b}\right]_{0.1\,\underline{N}\ CaCl_2}$$

$$= \left(\frac{\gamma_B^b}{\gamma_A^a}\right)_{0.1\ \underline{N}\ CaCl_2} K_{A\ 0.1\ N.\ CaCl_2}^B \qquad \text{(A-3)}$$

Since the thermodynamic selectivity coefficient is independent of reference solution, the above specific expression can be equated to the general expression giving,

$$\left(\frac{\gamma_B^b}{\gamma_A^a}\right)_{0.1\ \underline{N}\ CaCl_2} K_A^B{}_{0.1\ \underline{N}\ CaCl_2} = \frac{\gamma_B^b\ (B)_s^b\ (A)_z^a}{\gamma_A^a\ (A)_s^a\ (B)_z^b}$$

Rearranging, the B ion loading can be expressed in terms of the A ion loading

$$(B)_z = \left[\frac{(\gamma_B^b/\gamma_A^a)}{(\gamma_B^b/\gamma_A^a)_{0.1\ \underline{N}\ CaCl_2}} \frac{(B)_s^b}{(A)_s^a} \frac{(A)_z^a}{K_A^B{}_{0.1\ \underline{N}\ CaCl_2}}\right]^{\frac{1}{b}} \quad (A\text{-}4)$$

Activity coefficients may be neglected in univalent-univalent exchange, but are necessary in univalent-divalent exchange. The activity coefficients can be predicted using Debye-Huckel theory. A sample calculation using the above expression to predict equilibrium zeolite loading is shown next.

To calculate the ammonium ion loading on clinoptilolite, the fact that the equivalent fractions of all the ions on the zeolite must sum to one is used:

$$(NH_4)_z + (Ca)_z + (Mg)_z + (K)_z + (Na)_z = 1 \quad (A\text{-}5)$$

where $(A)_z$ represents the equivalent fraction of the cation exchange capacity of the zeolite occupied by ion A.

From typical simulated secondary effluent (SSE) specifications in Table A-1

$$\frac{(Na)_s}{(NH_4)_s} = 4.75 \qquad \frac{(K)_s}{(NH_4)_s} = 0.317$$

$$\frac{(Ca)_s}{(NH_4)_s^2} = 2083 \qquad \frac{(Mg)_s}{(NH_4)_s^2} = 1458$$

where $(A)_s$ = normality of ion A in solution.

From Debye-Huckel theory[5], the activity coefficient of ion i is:

$$\log_{10} \gamma_i = -0.509\ (Z_i^2)\ \sqrt{I}$$

$$I = 1/2\ \Sigma M_i\ Z_i{}^2\ ,\quad I \text{ is ionic strength}$$

TABLE A-1

SIMULATED SECONDARY EFFLUENT, SSE

Cations	Concentration, mg/l	Normality
Na^{+}	130	5.7×10^{-3}
K^{+}	15	3.8×10^{-4}
NH_4^{+}	20	1.2×10^{-3}
Ca^{+}	60	3.0×10^{-3}
Mg^{++}	25	2.1×10^{-3}

M_i = concentration gram ions/liter of ion i

Z_i = charge on ion i

for SSE

$Na^+ = 5.70 \times 10^{-3}$

$K^+ = .38 \times 10^{-3}M$

$NH_4^+ = 1.20 \times 10^{-3}M$

$Ca^{++} = 1.50 \times 10^{-3}M$ (1/2 normality)

$Mg^{++} = 1.05 \times 10^{-3}M$ (1/2 normality)

$Cl^- = 12.4 \times 10^{-3}M$ (assuming that Cl^- is the only negative ion)

for SSE

$I = 0.0149$

Using the Debye-Huckel relationship

$$\log_{10} \gamma_{Ca^{++}} = -0.509\ (2)^2\ \sqrt{0.0149}$$

$$\gamma_{Ca^{++}} = 0.564$$

$$\log_{10} \gamma_{NH_4^+} = -0.509\ (1)^2\ \sqrt{0.0149}\ ,$$

$$\gamma_{NH_4^+} = 0.868$$

For ~0.1 N $CaCl_2$ solution used to determine selectivity coefficients (NH_4^+ in the equilibrium solucion can be neglected),

$$I = 1/2\ [(0.05)\ (2)^2 + (0.1)\ (1)^2]$$

$$I = 0.15$$

$$\log_{10} \gamma_{Ca^{++}} = -0.509\ (2)^2\ \sqrt{0.15}$$

$$\gamma_{Ca^{++}} = 0.162$$

$$\log_{10} \gamma_{NH_4^+} = -0.509\ (1)^2\ \sqrt{0.15}\ ,$$

$$\gamma_{NH_4^+} = 0.635$$

$$\frac{\left(\frac{\gamma_{Ca^{++}}}{(\gamma_{NH_4^+})^2}\right)_{SSE}}{\left(\frac{\gamma_{Ca^{++}}}{(\gamma_{NH_4^+})^2}\right)_{0.1\ \underline{N}\ CaCl_2}} = \frac{0.747}{0.41} = 1.83$$

This factor of 1.83 is the correction factor between the SSE solution and the 0.1 N solution used to determine the values of the selectivity coefficient, $K^{Ca}_{NH_4}$.

Since Mg^{++} has the same charge as Ca^{++}, we will assume that the correction factor for $K^{Mg}_{NH_4}$ is also 1.83. Univalent-univalent exchanges will not require an activity correction. Using equation A-4,

$$K^{Na}_{NH_4\ 0.1\ \underline{N}\ CaCl_2} = 11, \quad (Na)_z = \frac{4.75}{11} (NH_4)_z$$

$$K^{K}_{NH_4\ 0.1\ \underline{N}\ CaCl_2} = 0.33, \quad (K)_z = \frac{0.317}{0.33} (NH_4)_z$$

$$K^{Ca}_{NH_4\ 0.1\ \underline{N}\ CaCl_2} = 760, \quad (Ca)_z = \frac{(2083)\ (1.83)}{760} (NH_4)^2$$

$$K^{Mg}_{NH_4\ 0.1\ \underline{N}\ CaCl_2} = 2400, \quad (Mg)_z = \frac{1458}{2400} (1.83) (NH_4)^2_z$$

Substituting in Equation A-5,

$$(NH_4)_z + 5.02\ (NH_4)^2_z + 1.11\ (NH_4)^2_z + 0.96\ (NH_4)_z + 0.43\ (NH_4)_z = 1 ,$$

$$2.39\ (NH_4)_z + 6.13\ (NH_4)^2_z - 1 = 0 ,$$

$$(NH_4)_z = \frac{-2.39 + \sqrt{5.71 + 2452}}{12.26} = 0.254$$

Since 1.81 meq/g is the total capacity of the zeolite

$$(.254)\ (1.81) = 0.46 \text{ meq/g}$$

compared to 0.4 meq/g determined experimentally.

APPENDIX B

PRELIMINARY DESIGN OF A 10 MGD AMMONIA REMOVAL PLANT UTILIZING ELECTROLYTIC RENOVATION OF SPENT REGENERANT

design of a plant using electrolysis for removal of ammonia from spent regenerant must be considered preliminary at this time due to ack of pilot scale data needed to optimize the operating parameters. service flow rates are the same as that (6 bv/hr) used in South oe's design of an air stripping lime regeneration process in Appendix C; ever, this flow rate is believed to be very conservative. No problems poor flow distribution because of solids plugging associated with the e of lime are anticipated. This is because the electrolysis process n be operated at neutral conditions. Laboratory data has indicated at flow rates up to 20 bv/hr can be used without significant leakage or emature breakthrough.

e capital cost of this installation is minimized through the use of inforced concrete tanks for the ion exchange beds rather than closed eel tanks as specified in South Tahoe's design. Further, open concrete nks will be acceptable with respect to ammonia volatilization in the lectrolysis process since very little ammonia will volatilize from the eutral regenerant solution. Where lime solids are a problem, the steel ressure tanks noted in Appendix C offer an advantage of quick removal nd cleaning of distribution screens. Fouling of the gravel underlayer f an open concrete tank would pose a serious problem of cleaning.

he ion exchange units are patterned after those used for water softening t the LaVerne Filtration Plant of the Metropolitan Water District of outhern California. The LaVerne units have been operated successfully ver a period of thirty years for softening Colorado River water. The largest ion exchange units presently used in the LaVerne Plant have a ross section of 1590 square feet. The ion exchange beds in this design ave a cross section of 800 square feet. This ammonia removal process employs four zeolite beds each containing 3200 cu ft of 20 x 50 mesh clinoptilolite. Three beds will be in service at any given time while the fourth bed will be undergoing regeneration. The zeolite beds will be operated in parallel to 150 bed volumes each before removal from service for regeneration. The service flow direction will be downflow and regeneration will be accomplished upflow. The relatively high density of the wet clinoptilolite granules (1.7 g/cm^3) will prevent localized fluidization or channeling during the upflow regeneration. The design specifies 15 volumes of neutral regenerant, which contains two equivalents per liter of mixed calcium, sodium, magnesium and potassium chlorides, for eluting the ammonia from the beds at 23°C. Laboratory elution data for a similar solution are given in Figure B-1 and shows almost 90% elution after 15 volumes of regenerant throughput. The evolution of heat during the

electrolysis step will increase the temperature of the regenerant, which is expected to increase the ammonium ion elution rate. However, no high temperature elution data are available to confirm a significant reduction in regenerant volume or regeneration time.

The regeneration step will require about 7.5 hours at 2 bv/hr. Regenerant will be pumped from the regenerant storage tank through the bed to the regenerant processing tank. At the end of the regeneration cycle, a rinse step will be initiated to push the remaining regenerant out of the zeolite voids to the regenerant processing tank. The regenerant in the processing tank will be pumped through a bank of electrolysis cells which generate chlorine for destruction of the ammonia. A flow diagram of the regeneration processing step is given in Figure B-2. A total of 530 cells, operating at about 6 volts and 500 amps, will be employed in the electrolysis of the spent regenerant. A lime slurry will be fed to the cell effluents to maintain a neutral pH. The regenerant will be pumped through an enclosed tank (50,000 gal) to capture the hydrogen evolved in the process. The hydrogen is vented to the atmosphere or burned. Approximately 7 cu ft of hydrogen gas will be generated from the destruction of ammonia in 1000 gallons of wastewater at an NH_3-N concentration of 15 mg/l. A 10 MGD plant will therefore be producing about 70,000 cu ft of hydrogen per day. The cost of recovering the hydrogen, including scrubbing to remove the nitrogen trichloride, is more than the thermal value of the hydrogen.

Figure B-3 illustrates the design of the reinforced concrete tanks for the zeolite beds. The beds are contained in tanks measuring 40 ft in length, 20 feet in width, and 8.25 ft in depth. The zeolite beds are 4 ft deep and are supported on 12 in of 4 layers of graded gravel. The total height of 8.25 ft allows for backwash and the distrbution system. The distribution system over the beds for regenerant draw-off and service feed consists of a trough running down the middle of the tank lengthwise with connecting troughs with overflow weirs running laterally, spaced 4 feet apart. The distribution system under the beds consists of the perforated concrete units of the type employed at the LaVerne plant.

Summaries of costs for a 10 MGD plant for treating tertiary effluent and using electrochemical renovation of the regenerant are shown in Tables B-1 and B-2. The estimates are patterned after those used by South Tahoe in Appendix C except where electrochemical renovation or the modifications discussed above require changes. One exception is that a flat 46% of capital is used to estimate auxiliaries, contingenices and engineering design. This is roughly equivalent to similar expenses which are itemized in Appendix C. Less make-up clinoptilolite is required than in the design in Appendix C because neutral operation will eliminate solids precipitation and the need for backwashing with the accompanying zeolite loss. Electrical energy for electrolysis was assumed to be 50 watt hours/g NH_3-N. The costs for lime and NaCl are the same as for the South Tahoe design. Although the chemistry is different, the net amount of lime required for neutralization is the same. Make-up NaCl is required to compensate for losses; there is no net consumption by the chemical reactions in either process.

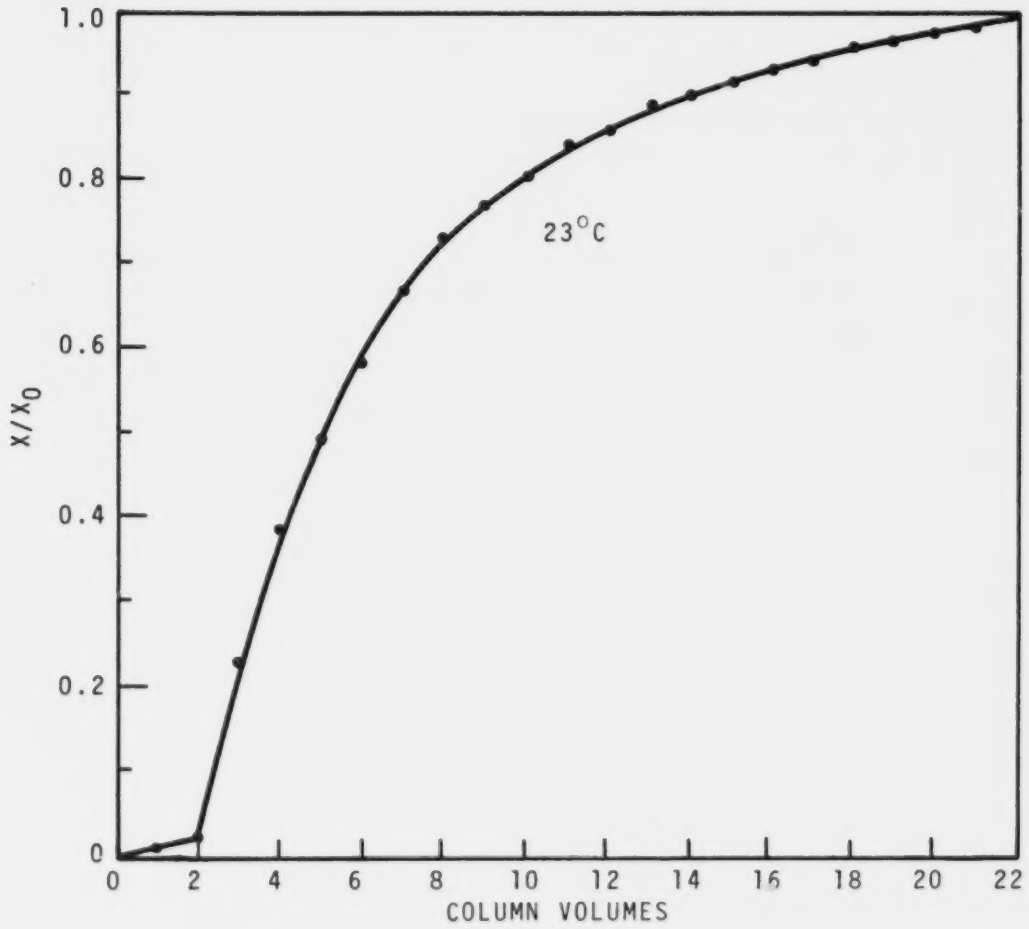

FIGURE B-1. ELUTION OF HECTOR CLINOPTILOLITE, 30 g, 20-50 MESH, LOADED WITH 1.2N NH_4CL + 0.83 N KCl, X_o = 37.3 MEQ NH_4^+/30 g COLUMN. SEVEN COLUMN VOLUMES/HR ELUTION RATE. ELUTING SOLUTION CONTAINED 0.1425 N NaCl + 0.0095 N KCl + 1.8747 N $CaCl_2$ + 1.3122 N $MgCl_2$. X/X_o = FRACTION ELUTED.

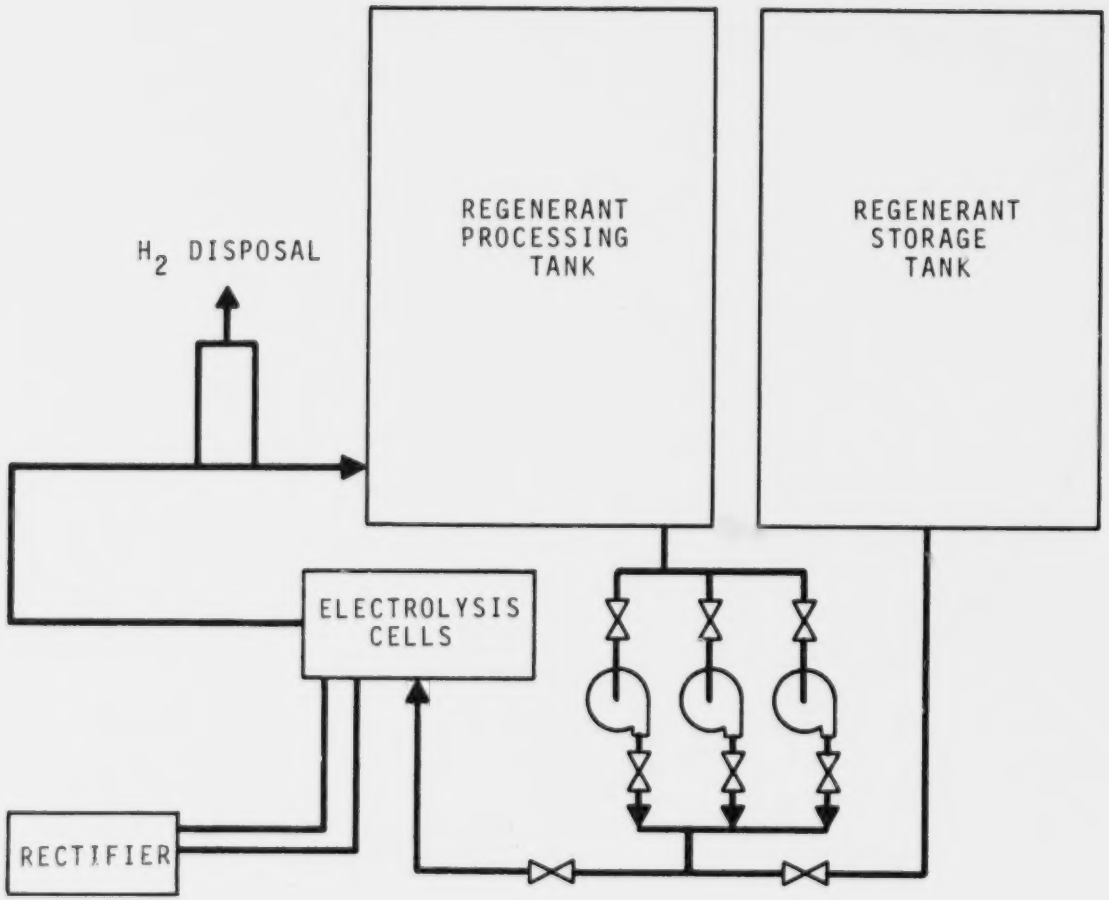

FIGURE B-2. REGENERANT PROCESSING FLOWSHEET

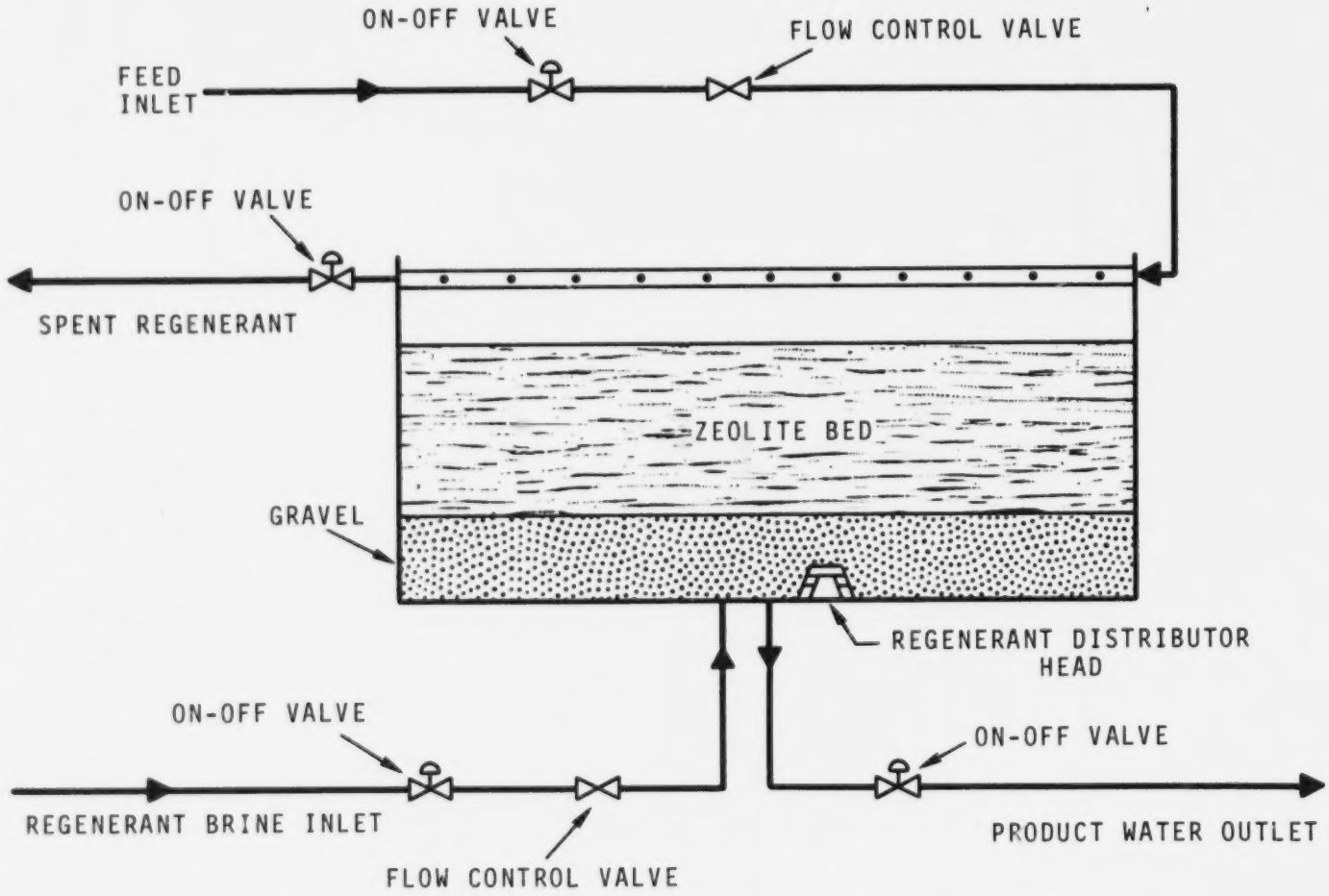

FIGURE B-3. TYPICAL VALVE ARRANGEMENT FOR ION EXCHANGE TANK

TABLE B-1

PRELIMINARY CAPITAL COSTS - ELECTROLYSIS PROCESS - 10 MGD

Description	Quantity	Total Cost
Electrolysis unit complete with cells, rectifier, piping and bus bars with 20% extra cells	636 cells	$ 420,000
Ion exchange beds with distribution system	4	48,000
Regenerant processing and storage tanks -- 500,000 gallon	2	96,000
Hydrogen recovery tank	1	28,000
Piping	-	139,000
Instrumentation	-	79,000
Valves	30	77,000
Regenerant processing pumps--15,000 gpm	3	17,000
Product water pumps--4,000 gpm	3	7,000
Regenerant-backwash pumps--6,000 gpm	3	9,000
Zeolite	12,400 cu ft	124,000
	Equipment Total	$1,044,000
Plus 46% auxiliary, contingencies and engineering design		480,000
	Total Capital Cost	$1,524,000

TABLE B-2

PRELIMINARY ESTIMATE OF TOTAL COST FOR ELECTROLYSIS PROCESS

	Cost/MG
Lime	$ 6.50
Make-up Sodium Chloride	6.90
Make-up Clinoptilolite	0.20
Chlorine	6.40
Electricity	42.80
Anode Replacement (2 yr life)	4.40
Operational Labor	14.00
Maintenance, Material and Labor	9.20
Total Operating Cost	90.40
Capital Amortization, 6% for 20 yr	36.40
Total Cost	$126.80

APPENDIX C

ENGINEERING DESIGN OF A 7.5 MGD AMMONIA REMOVAL PLANT UTILIZING AIR STRIPPING FOR RECOVERY OF SPENT REGENERANT

This appendix presents an engineering design report prepared by the South Tahoe Public Utility District, South Lake Tahoe, California. Experimental data used in the design, and discussed in preceding sections, were obtained when Battelle's mobile pilot plant was located at South Lake Tahoe. This design was for a plant utilizing air stripping to remove ammonia from the clinoptilolite regenerant. The report is appended here to combine designs with alternate approaches to regenerant recovery in a single publication.

The Environmental Protection Agency (EPA) should be substituted for the Federal Water Quality Administration (FWQA) in the following report.

PHASE I - ENGINEERING DESIGN REPORT

SUPPLEMENTING AMMONIA STRIPPING WITH FURTHER NITROGEN REMOVAL BY SELECTIVE ION EXCHANGE AND BREAKPOINT CHLORINATION

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for the

FEDERAL WATER QUALITY ADMINISTRATION

Program #17010 EEZ
Contract #14-12-561
FWQA Project Officer, Dr. R. B. Dean
Advanced Waste Treatment Research Laboratory
Cincinnati, Ohio
April, 1970
Project No. L-145.98

ABSTRACT

Pilot plant investigations of the efficiency of nitrogen removal from a tertiary treated sewage effluent were conducted at the South Tahoe Public Utility District. The nitrogen removal process utilized ion exchange and employed a natural zeolite, clinoptilolite, which is selective of ammonium ions in the presence of sodium, magnesium, and calcium ions. Regeneration of the exhausted clinoptilolite is accomplished with solutions or slurries containing lime. Lime provides hydroxyl ions which react with the ammonia ions to yield an alkaline aqueous ammonia solution. The ammonia solution is processed through a heated air stripping tower to remove the ammonia which is exhausted harmlessly to the atmosphere. The regenerant solution is not discarded and the process generates no liquid wastes. Ammonia removals as high as 99% can be obtained using this process.

The pilot plant investigation provided the design criteria on which a preliminary design of a 7½ mgd plant is based. The plant design provides a system utilizing 12 exchange beds, nine of which are in service at all times, and three of which are in a regenerant cycle. Each bed would be 12 feet in diameter and have an effective clinoptilolite depth of 8 feet. The flow through the bed would be 6 bed volumes per hour or 680 gpm.

The construction and operating costs of the 7½ mgd plant are estimated. Based on current costs in the Lake Tahoe region, the process is estimated to cost $84.95 per million gallons to operate, and capital costs amortized at 6% interest for 20 years are estimated to be $63.10 per million gallons.

This report was submitted in fulfillment of Contract 14–12–561 (17010 EEZ) between the Federal Water Quality Administration and the South Tahoe Public Utility District.

Key Words: Nitrogen Removal, Ion Exchange, Clinoptilolite, Ammonia Stripping, Tertiary Treatment Costs.

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5	SECTIONS & DETAILS

INTRODUCTION

The potential benefits of removing nitrogen from wastewaters are well known and will not be recited here in detail. The principal benefits from nitrogen removal to a low residual include restriction of algal growths, and elimination of the toxic effects of ammonia nitrogen on fish and aquatic life. Ammonia removal also enhances the efficacy of chlorination in disinfection of wastewaters.

Today, advanced wastewater treatment processes are developed to the extent that practical, reliable, and plant-proven methods are available to produce reclaimed water of such high quality that it may be used for any desired purpose.

The costs are reasonable too, with two notable exceptions, the costs for nitrogen removal and for dewatering of sewage-chemical sludge mixtures. The latter problem can be avoided by separate settling and handling of sewage sludge and chemical sludge in those situations where the mixture is too expensive to dewater. Also, it is possible that methods may be developed to cut the cost for handling difficult sludge mixtures.

Unfortunately, there does not appear to be in the offing a solution to the high cost of nitrogen removal. Ammonia stripping is by far the cheapest means of nitrogen removal which has, at this time, a high degree of reliability and ease of control. However, ammonia stripping is subject to considerable loss of efficiency at water and air temperatures near freezing, and it is not practical to operate the process at all at air temperatures below freezing.

Deposition of scale on stripping tower packing is a problem at present, but it appears probable that this problem can be solved. Assuming solution of the calcium carbonate deposition problem, which appears likely, then ammonia stripping may be a good method for nitrogen removal in warm climates. It could be supplemented by breakpoint chlorination where required to remove residual ammonia following stripping.

In cold climates it is undoubtedly still economical to use ammonia stripping at air temperatures above freezing, provided it can be supplemented at temperatures slightly above freezing and supplanted entirely by another method of nitrogen

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removal at air temperatures below freezing. This project was undertaken with this approach in mind. The existing ammonia stripping tower was to be supplemented or supplanted, according to air temperatures, by the selective ion exchange process for the removal of ammonia nitrogen from wastewater as developed to the pilot plant stage by Battelle-Northwest under contract to FWQA. The process employs a natural zeolite, clinoptilolite, which is selective of ammonium ions in the presence of sodium, magnesium, and calcium ions. Regeneration of the exhausted clinoptilolite is accomplished with solutions or slurries containing lime. Lime provides hydroxyl ions which react with the ammonium ions to yield an alkaline aqueous ammonia solution. This ammonia solution is processed through a heated air stripping tower to remove the ammonia which is exhausted harmlessly to the atmosphere. The spent regenerant is then fortified with more lime and recycled to the zeolite bed to remove more ammonia. Since the regenerant is not discarded, the process generates little liquid wastes. Ammonia removals as high as 99% can be obtained using this process. The last 0.5 to 1.0 mg/l of ammonia nitrogen can then be removed by use of breakpoint chlorination. Battelle-Northwest has constructed a 100,000 gpd mobile demonstration plant for further study of this process. They very kindly conducted tests over a period of several months last year at the Tahoe plant. The results of their pilot plant work on the Tahoe reclaimed water established the design criteria for the full-scale plant on which this report is based.

Phase I of the contract with FWQA consists of the preparation of an engineering design report. Phase II is the construction of full-scale plant facilities using selective ion exchange for supplemental nitrogen removal. Phase III covers collection, analysis, and reporting of data on the efficiency and cost of nitrogen removal by ion exchange, ammonia stripping, and breakpoint chlorination, for a 2-year operational period.

This report completes Phase I of the project, and gives a basis for consideration of proceeding with Phase II. It presents the design criteria developed by Battelle-Northwest in their pilot plant work as applied to a preliminary design of a full-scale plant for ammonia removal by selective ion exchange. The description of the proposed plant is illustrated by drawings showing the general layout and design of the facilities. Cost estimates are also presented. The proposed plant has been designed for a nominal capacity of 7½ mgd, which corresponds to that of the existing advanced wastewater treatment plant. The decision to build a 7½-mgd plant addition is based upon several important considerations. First, it has been observed

that most of the great number of visitors who tour the plant and export facilities, as well as local residents, judge the accomplishments of the plant almost solely on the quality of the final effluent as represented by the appearance of the Indian Creek Reservoir. If only part of the plant flow is treated, then the quality of the reclaimed water as produced by the plant does not truly reflect the process capabilities. This is not just an idea, it is a fact which has already been driven home as a result of experience with the ammonia stripping tower which has a capacity of only one-half that of the rest of the plant. This means even during low flow seasons, that part of the plant flow must be bypassed during maximum hourly flows. Test data can be gathered under these conditions, but the value of plant scale demonstration is completely lost, or even becomes negative, so far as visitor impressions are concerned. We are of the firm opinion that a successful plant scale demonstration absolutely requires that the capacity of all facilities be built to full 7½-mgd capacity. There is more than visitor impressions involved. Indian Creek Reservoir is being intensively studied so far as algal grówths are concerned. Since the reservoir is drained down to about one-third full capacity each summer for irrigation purposes, it is possible to test under natural conditions the effects of nitrogen removal. Actually, phosphorus reductions to a residual of about 0.1 mg/l have given excellent control of algal growths in the reservoir. Against this background of field data, further possible benefits from nitrogen removal can be evaluated.

PROPOSED PROCESS AND DESIGN CRITERIA

Process Description

The selective ion exchange process developed by Battelle-Northwest[1] for removal of ammonia nitrogen from wastewater is the basis for a proposed full-scale plant at the South Tahoe Water Reclamation Plant.

The process employs a natural zeolite, clinoptilolite, which is selective for ammonium ions in the presence of sodium, magnesium, and calcium ions.[2] A high pH lime solution containing NaCl and $CaCl_2$ is used to regenerate the exhausted clinoptilolite. The solution provides both ions for exchange with the ammonium ions and hydroxyl ions to yield an alkaline aqueous ammonia solution. The following equation approximates this reaction:

$$2NH_4^{+1}R^{-1} + Ca(OH)_2 \longrightarrow Ca^{+2}R_2^{-1} + 2NH_3 + 2H_2O$$

The presence of a significant amount of sodium on the clinoptilolite lengthens the service cycle and shortens the elution cycle.

After the ammonium ion is eluted from the clinoptilolite, the high pH alkaline aqueous ammonia solution is passed through an air stripping tower where the ammonia is stripped from the regenerate or elutrient. Make-up lime and salt are added to replace the exchanged calcium and sodium.

At the South Tahoe Water Reclamation Plant, the proposed clinoptilolite exchange process would be added to the existing plant following the carbon adsorption step as shown on Drawing No. 1. The quality of the water, see Table A, is such as to preclude organic fouling of the ion exchange beds.

A schematic diagram of the proposed ion exchange beds, lime elutrient system, and ammonia air stripping system is shown on Drawing No. 2. For design flows, nine beds would be in service and three beds in regeneration.

The direction of flow for the beds in service would be downflow. All beds would operate in parallel.

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(1) Developed by Battelle Memorial Institute, Pacific Northwest Laboratories Division, under contract with the Federal Water Pollution Control Administration.

(2) Battelle-Northwest, "Research Report, Ammonia Removal from Agricultural Runoff and Secondary Effluents by Selective Ion Exchange to the FWPCA," December 1968, 56 p.

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Table A

Typical Carbon Column Effluent Quality
Before Chlorination

BOD (mg/l)	1 - 2
COD (mg/l)	5 - 15
Turbidity (JU)	0.3 - 0.8
MBAS (mg/l)	0.1 - 0.2
pH	7.0 - 8.0
Coliforms (mpn/100ml)	less than 50
Nitrogen (mg/l-N)	
Ammonia	4 - 20
Nitrite	0.1 - 0.6
Nitrate	1 - 2
Suspended Solids (mg/l)	-0-
Total Dissolved Solids (mg/l)	250 - 350
Phosphorus (mg/l PO_4-P)	0.05 - 0.15
Alkalinity (mg/l $CaCO_3$)	150 - 250
Hardness (mg/l $CaCO_3$)	50 - 175
Chlorides (mg/l)	25
Sulfates (mg/l)	25
Carbon Fines	some present

When a given volume of carbon column effluent has passed through a set of three beds, for example, beds 1, 2, and 3, this set of beds would be taken off line for regeneration. At this time, from a previous regeneration, elutrient tank A would contain elutrient water with a very high ammonia content (say 600 mg/l), tank B would contain elutrient water with a low ammonia content (say 100 mg/l), and tank C would contain ammonia-free elutrient water (say 10 mg/l). The contents of tank A would be air stripped during the regeneration of exchange beds 1, 2, and 3. The regeneration would proceed as follows:

1. Exchange beds 1, 2, and 3 would be drained to the final effluent.

2. Low ammonia content elutrient water from tank B (100 mg/l) would be recirculated upflow through the three exchange beds and back through tank B to the exchange beds until the concentration of ammonia in the elutrient began to approach a maximum value (say 600 mg/l). Throughout the recirculation, make-up lime and salt would be added. A pH of about 11.5 would be maintained.

3. After an allotted time (long enough for elutrient from tank B to approach a maximum ammonia concentration, the elutrient would be changed to recirculation to and from tank C through beds 1, 2, and 3. Tank C with its ammonia-free elutrient water would be recirculated for an allotted time (long enough for elutrient from tank C to reach about 100 mg/l). At this stage of the elution, the small amount of ammonia left on the zeolite would be distributed uniformly throughout the bed. Tank A with ammonia-free water (10 mg/l NH_3, water stripped during the regeneration of beds 1, 2, 3) would be pumped once upflow through the bed to further polish the lower portion of the bed and prevent leakage of ammonia during the downflow service cycle.

The elutrient in tank B (600 mg/l - NH_3) would be held for air stripping during the regeneration of the next set (say beds 4, 5, and 6) of ion exchange beds. Tank C with 100 mg/l elution water would become the lead tank for this next set of ion exchange beds. Tank A with ammonia-free elution water (10 mg/l - NH_3, water stripped during the regeneration of beds 1, 2, 3) would be used as the polishing tank for beds 4, 5, and 6.

4. Once the elution of beds 1, 2, and 3 was completed, the three beds would be drained back to tank A.

5. Beds 1, 2, and 3 would then be filled slowly (from the bottom to remove trapped air) with product water from the other nine beds in service.

6. After the beds were filled with product water, more product water would be pumped at a high rate through beds 1, 2, and 3 in sequence. The backwash water would be routed through the sludge line to the floc basin, which is located just ahead of the chemical clarifier in the existing plant. (See Drawing No. 3)

7. After backwashing was completed, ion exchange beds 1, 2, and 3 would be placed in service and beds 4, 5, and 6 would be taken off line for regeneration.

Ammonia in the elutrient solution would be removed by air stripping at a pH of about 11.5. In the preceding example, during the regeneration of beds 1, 2, and 3, the very high ammonia content (600 mg/l) in the elutrient solution of tank A was to be air stripped. The following procedure would be used:

1. The contents of tank A would pass through the tower down into the recycle basin below the tower.

2. The contents of the recycle basin would then be pumped back up through the tower once again. This time, however, the effluent from the tower would flow back to tank A.

3. The contents of tank A would now contain about 10 mg/l of ammonia, and would be ready to serve as the polishing volume during the regeneration of ion exchange beds 4, 5, and 6;

Breakpoint Chlorination

In order to remove the last 0.5 - 1.0 mg/l NH_3-N remaining after treatment with clinoptilolite, breakpoint chlorination would be accomplished just prior to pumping the reclaimed water to Luther Pass. No new equipment is needed for this purpose, as the existing chlorinators are adequate.

Design Criteria

Phase I of the District's research contract with the FWQA includes the collection of pilot plant data using the Battelle-Northwest mobile pilot plant and carbon column effluent from the reclamation plant. The data are used in preparing this report.

A summary of the design criteria based on the pilot work accomplished September through December 1969 is listed in Table B.

TABLE B

PROPOSED DESIGN CRITERIA – AMMONIA REMOVAL BY SELECTIVE ION EXCHANGE AND BREAKPOINT CHLORINATION AT THE SOUTH TAHOE WATER RECLAMATION PLANT

Capacity	7.5 mgd
Ammonia Concentration	
Influent	15-20 mg/l NH_3-N
Ion Exchange Effluent	0.5-1.0 mg/l NH_3-N
Chlorinated Effluent	0 mg/l NH_3-N
Exchange Beds	
Length of Service Cycle	150 bv (1)
Service Cycle Loading	6 bv/hour
Bed Depth	8 ft
Bed Diameter	12 ft
Exchange Bed Regeneration	
Quantity of Elutrient	8 bv
Elution Rate	10 bv/hr
Elutrient (Initial – Ca build-up during service)	
Calcium Oxide	500 mg/l
Sodium Chloride	2.0 N
pH	11.5
Ammonia Stripping Tower	
Capacity	300 gpm
Air/Water Ratio	300 cfm/gpm
Hydraulic Loading	3.5 gpm/ft^2
Packing Height	24 ft
Efficiency per Pass	85%
Number of Passes	2
Temperature	
Elutrient	74°
Stripping Tower Air	74°
Breakpoint Chlorination	10 mg Cl_2/mg NH_3-N

(1) bv means gross bed volumes

PILOT PLANT STUDIES

Service Cycle

Pilot scale studies on ammonia removal from South Tahoe Public Utility District tertiary effluent by selective ion exchange were conducted over a 4-month period with a 100,000-gpd mobile pilot plant. This plant has three 500-gallon ion exchange vessels (3.25 ft in diameter by 8 ft high) which were filled with 38 ft^3 (284 gal) to 50 ft^3 (374 gal) of the natural zeolite, clinoptilolite. Feed water was percolated through the zeolite beds either singly or in series until ammonia breakthrough occurred. The beds were regenerated with solutions containing lime, NaCl and $CaCl_2$. The spent regenerant containing ammonia was recovered for reuse by air stripping the ammonia from the regenerant solution in a 3.6 ft diameter by 8 ft column packed with one-inch polypropylene Intalox (R) saddles. The flow rate to the stripping column was normally 20 gpm with an air/liquid ratio of 150 cfm/gpm. Ammonia removal in the air stripper averaged about 40% at 25°C. The spent regenerant was normally recycled through the air stripper and zeolite bed until the NH_3-N concentration in the stripped regenerant was reduced to 10 mg/l.

Zeolite ammonia loading studies were carried out to establish the volume of feed water that can be processed through a zeolite bed until significant ammonia breakthrough occurred. The computed NH_3-N loading on two 4.5 ft beds of zeolite (9 ft total bed depth) with South Tahoe Public Utility District tertiary effluent containing 12 mg/l NH_3-N was 6.52 g of NH_3-N per gallon of zeolite. The average NH_3-N concentration in the effluent was approximately 0.4 mg/l at a flow rate of 4.2 bed volumes per hour. On this basis the volume processed for the 9-ft bed was 150 bed volumes. The volume selected for full-scale plant design is 150 bed volumes at a flow rate of 6 bed volumes per hour with a 12-foot-diameter bed, 8 feet in depth. An average effluent NH_3-N concentration of 0.5 to 1.0 mg/l is expected under these conditions, with 15-20 mg/l NH_3 in the influent.

Figure 1 illustrates NH_3-N breakthrough curves for a single 6-foot bed of zeolite operated at flow rates varying from 6.5 to 9.7 bed volumes per hour with 15 to 17 mg/l NH_3-N in the influent. Curve 1 at 8.1 bed volumes per hour shows the lowest average effluent NH_3-N concentration (0.67 mg/l) to 150 bed volumes but also has the lowest average influent NH_3-N concentration (15 mg/l). Curve 2 at 6.5 bed volumes per hour shows an average of 0.83 mg/l NH_3-N in 150 bed volumes of

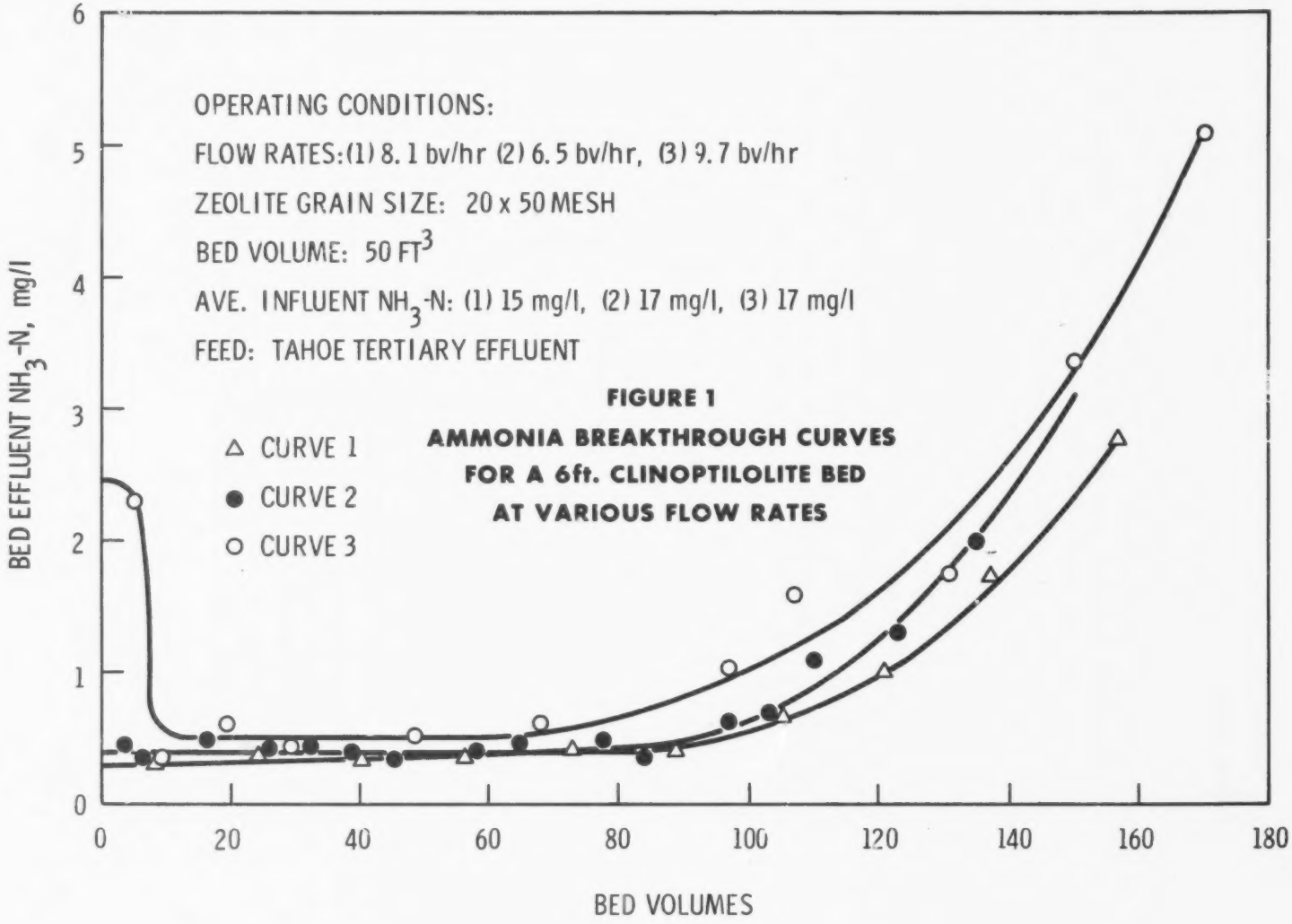

FIGURE 1
AMMONIA BREAKTHROUGH CURVES FOR A 6ft. CLINOPTILOLITE BED AT VARIOUS FLOW RATES

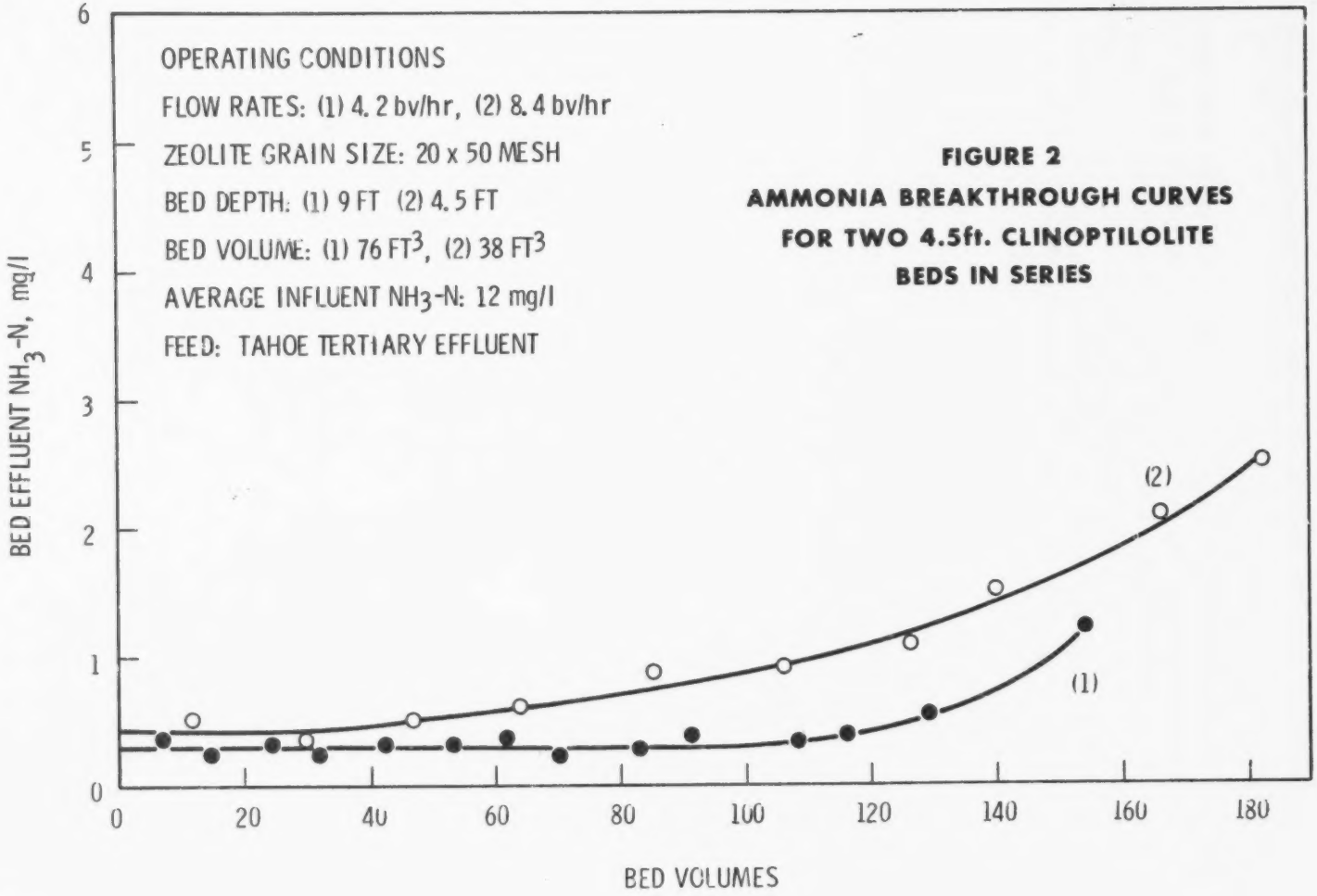

FIGURE 2
AMMONIA BREAKTHROUGH CURVES FOR TWO 4.5ft. CLINOPTILOLITE BEDS IN SERIES

effluent with an influent containing an average of 17 mg/l NH_3-N. Curve 3 at 9.7 bed volumes per hour shows an average effluent NH_3-N concentration of 1.2 mg/l NH_3-N. Curve 3 also shows an initial high NH_3-N concentration which is the result of insufficient backwash removal of residual lime remaining in the bed after regeneration.

Ammonia-nitrogen breakthrough curves for two 4.5-foot zeolite beds operated in series are illustrated in Figure 2. The average NH_3-N concentration in 150 bed volumes from the first bed in series (Curve 2) was 0.81 mg/l at a flow rate of 8.4 bed volumes per hour. The average NH_3-N concentration in the effuent from the second zeolite bed (Curve 1) (total 9-foot bed depth) was 0.35 mg/l at a flow rate of 4.2 bed volumes per hour. The average NH_3-N concentration in the influent was 12 mg/l.

It is evident from the data above and from series operation data that the higher influent NH_3-N concentrations will produce higher effluent NH_3-N values. Breakthrough and leakage are influenced by bed packing characteristics and are subject to variation, other factors being equal. In general, deep beds at low flow rates will yield the low leakage and sharp breakthrough curves.

Elution Cycle

In order to minimize the volume of regenerant required to elute the NH_3-N from the zeolite beds, a batch regeneration technique was studied. A minimum volume of regenerant is desired to maintain a low heat input during the air stripping operation in cool weather. Pilot plant data show that the NH_3-N concentration in recycled regenerant increases rapidly from near zero to about 500 mg/l in a few hours with a zeolite bed loaded with an average of 8.5 g of NH_3-N per gallon of bed. Three elution curves are illustrated in Figure 3 for average bed loading of 8.5 g of NH_3-N per gallon of bed. Curve 1 shows the lowest NH_3-N (450 mg/l) concentration after 6 hours, which is believed to be the result of the low pH (10.8). The NH^{+4} concentration at 450 mg/l NH_3-N and pH 10.8 is 8.9×10^{-4}M compared with 4.0×10^{-4}M NH^{+4} at pH 11.2 and 500 mg/l NH_3-N and 2.1×10^{-4}M NH^{+4} at pH 11.5 and 520 mg/l NH_3-N. The amount of ammonia removed from the zeolite will, therefore, increase with pH (low solution NH^{+4} concentrations show low NH^{+4} zeolite adsorption). Curve 2 shows a slower rate of elution of the regenerant solution than curve 3, which is believed due to a combination of the slower flow rate and lower temperature and pH. Curve 3 shows that equilibrium was attained after 4.5 hours.

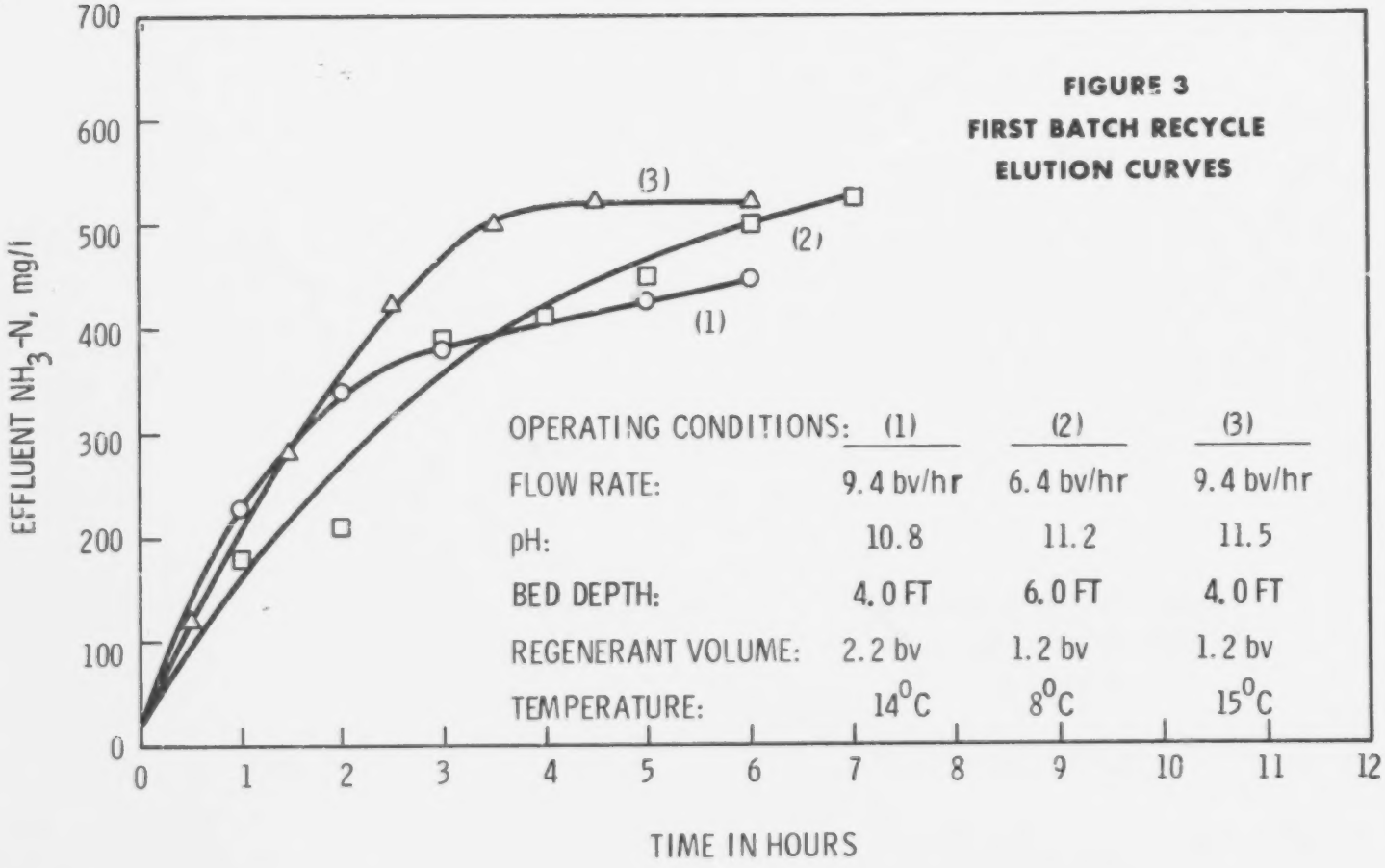
FIGURE 3
FIRST BATCH RECYCLE
ELUTION CURVES
EFFLUENT NH_3-N, mg/l
TIME IN HOURS
(1)
(2)
(3)
OPERATING CONDITIONS: (1) (2) (3)
FLOW RATE: 9.4 bv/hr 6.4 bv/hr 9.4 bv/hr
pH: 10.8 11.2 11.5
BED DEPTH: 4.0 FT 6.0 FT 4.0 FT
REGENERANT VOLUME: 2.2 bv 1.2 bv 1.2 bv
TEMPERATURE: 14°C 8°C 15°C

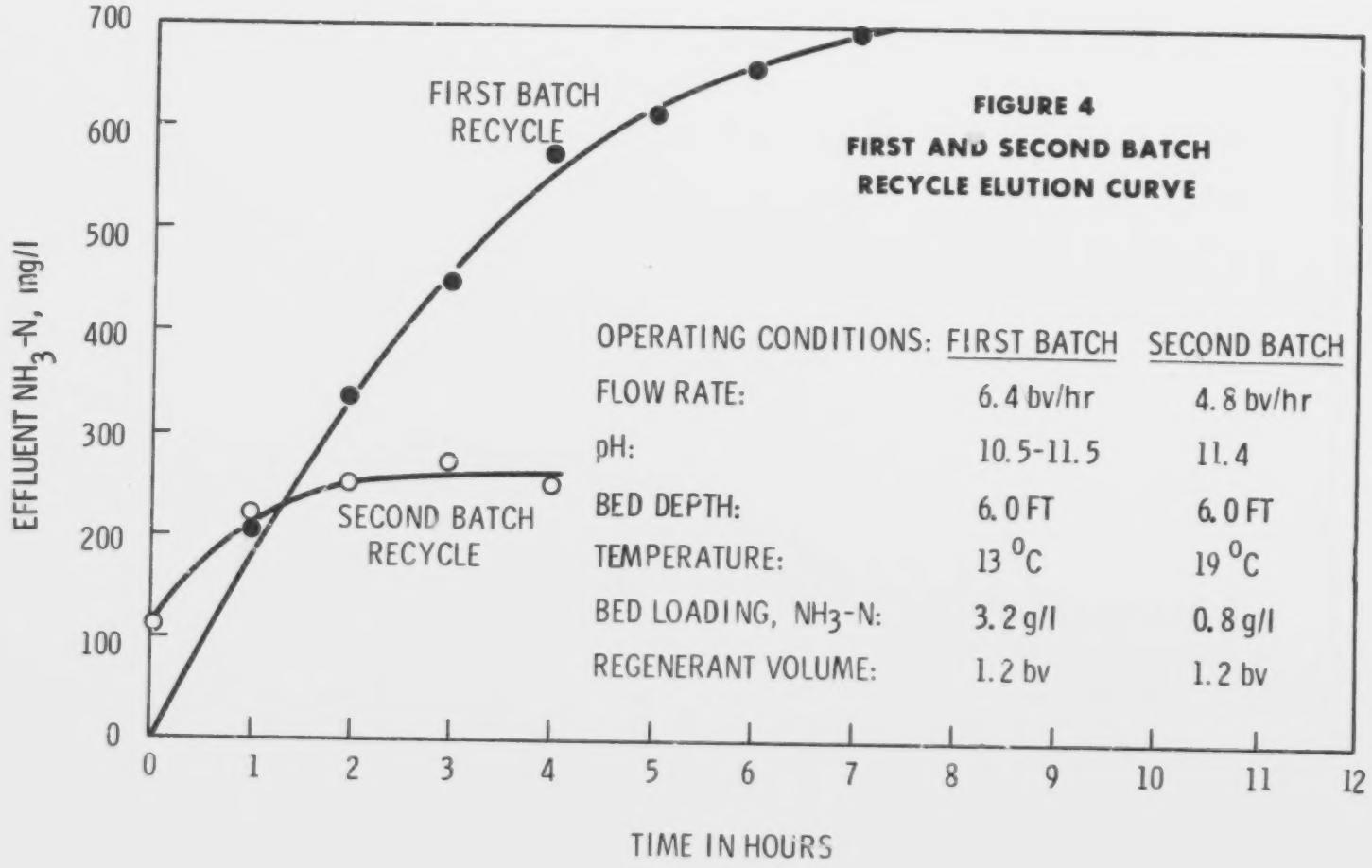

FIGURE 4
FIRST AND SECOND BATCH RECYCLE ELUTION CURVE

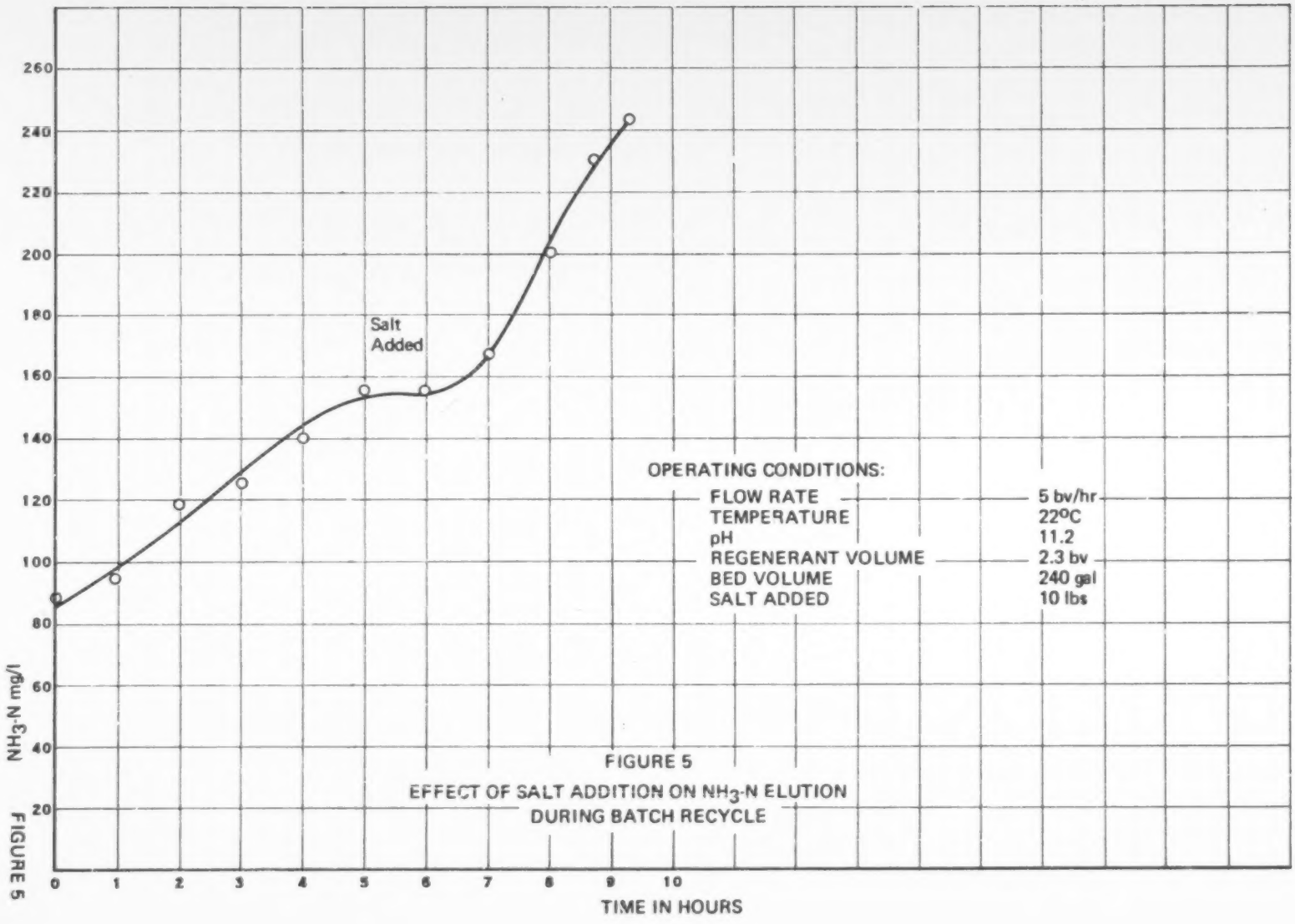

FIGURE 5

EFFECT OF SALT ADDITION ON NH_3-N ELUTION DURING BATCH RECYCLE

Curves 1 and 3 represent the recycle of 2.2 bed volumes; whereas, curve 2 represents 1.2 bed volumes. In order to attain a sufficiently high NH_3-N removal, the recycle of 4 bed volumes of regenerant is recommended at pH 11.5 with regenerant containing 0.2M Na^+ plus 1M Ca^{+2} which is in equilibrium with the Na^+. At 500 mg/l removal in the 4 bed volumes of recycled regenerant (average loading of 10 g of NH_3-N per gallon of zeolite), the first batch recycle will elute 75% of the loaded NH_3-N.

The second batch recycle is expected to bring the elution up to more than 90% and will contain about 100 mg/l NH_3-N. Since the second batch recycle is used without air stripping for the first batch recycle of the next regeneration, it then will attain an ultimate NH_3-N concentration of 600 mg/l at 75% elution. Figure 4 illustrates a first and second batch recycle for a highly loaded zeolite bed (3.2 g of NH_3-N per liter of bed). The first batch was air stripped to 107 mg/l NH_3-N while recycling through both the zeolite bed and the stripping column. Regeneration was 75% complete at this point. The NH_3-N increased by 150 mg/l in the regenerant after 2 hours in the second batch recycle, which indicates that the regeneration will be close to 100% with 4 bed volumes. The time required for the second batch recycle (2 hours) was less than that of the first batch (4-6 hours) due to : (1) The time lag in reaching the optimum pH at the beginning of the first batch recycle and; (2) the lower temperature of the first batch recycle (9°C vs 19°C).

The effect of salt (NaCl) addition during a batch recycle is illustrated in Figure 5. The salt was added when the NH_3-N concentration in the regenerant appeared to be leveling off at 155 mg/l. The NH_3-N concentration then increased at a rate higher than that prior to the salt addition. The loss in regenerant per cycle is about 5% of a bed volume based on laboratory data which is approximately 1.3% of 4 bed volumes of regenerant. The total salt lost per thousand gallons of water treated is estimated to be 0.32 lbs of NaCl from a regenerant solution containing mixed salts ($CaCl_2$ + NaCl) at a concentration of 2.2 equivalents per liter. The maximum pH that can be attained by adding lime to this regenerant is 11.5.

Ammonia Stripping Tower

The design criteria for the ammonia stripping tower were based on pilot plant studies by the South Tahoe Public Utility District.(1) Figures 6 and 7 indicate that 85% removal at 74°F can be achieved with an air-to-liquid ratio of 300 cfm/gpm and a surface loading of 3.5 gpm/ft^2 in a 24 ft tower.

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(1) Smith and Chapman, "Recovery of Coagulant, Nitrogen Removal, and Carbon Regeneration in Waste Water Reclamation," FWPCA Grant WPD-85, June 1967.

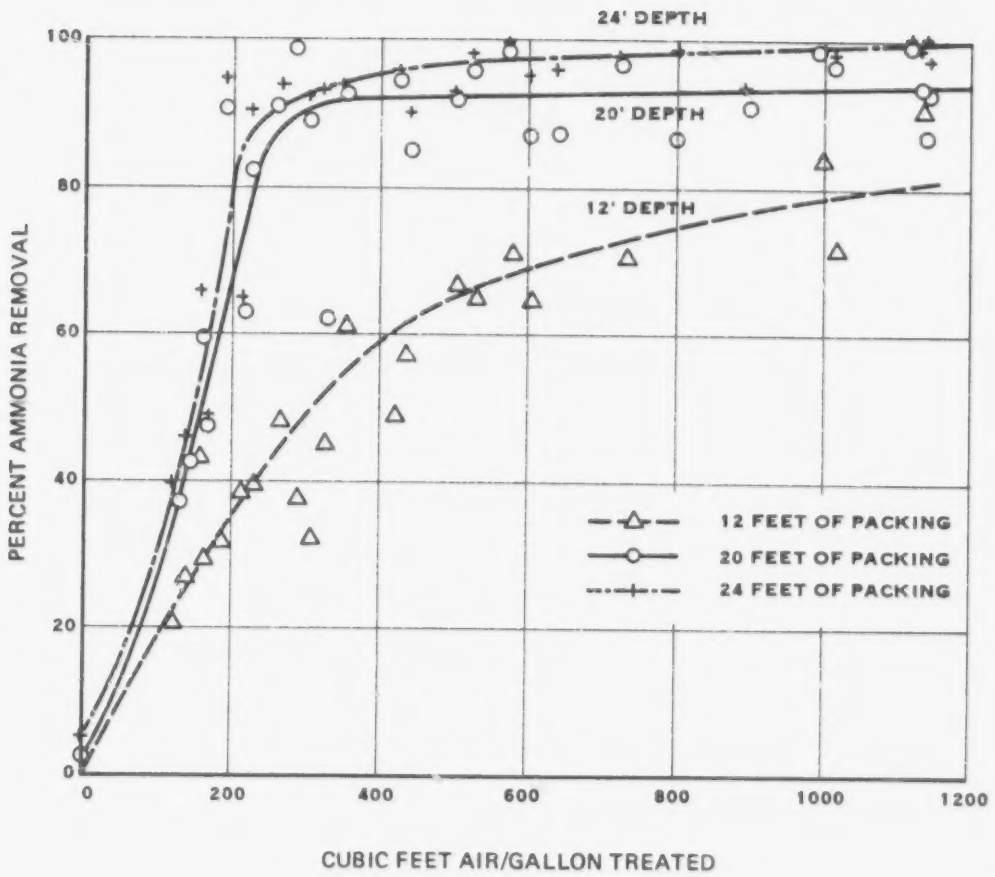

FIGURE 6
PERCENT AMMONIA REMOVAL VS CUBIC FEET
OF AIR PER GALLON WASTEWATER TREATED
FOR VARIOUS DEPTHS OF PACKING

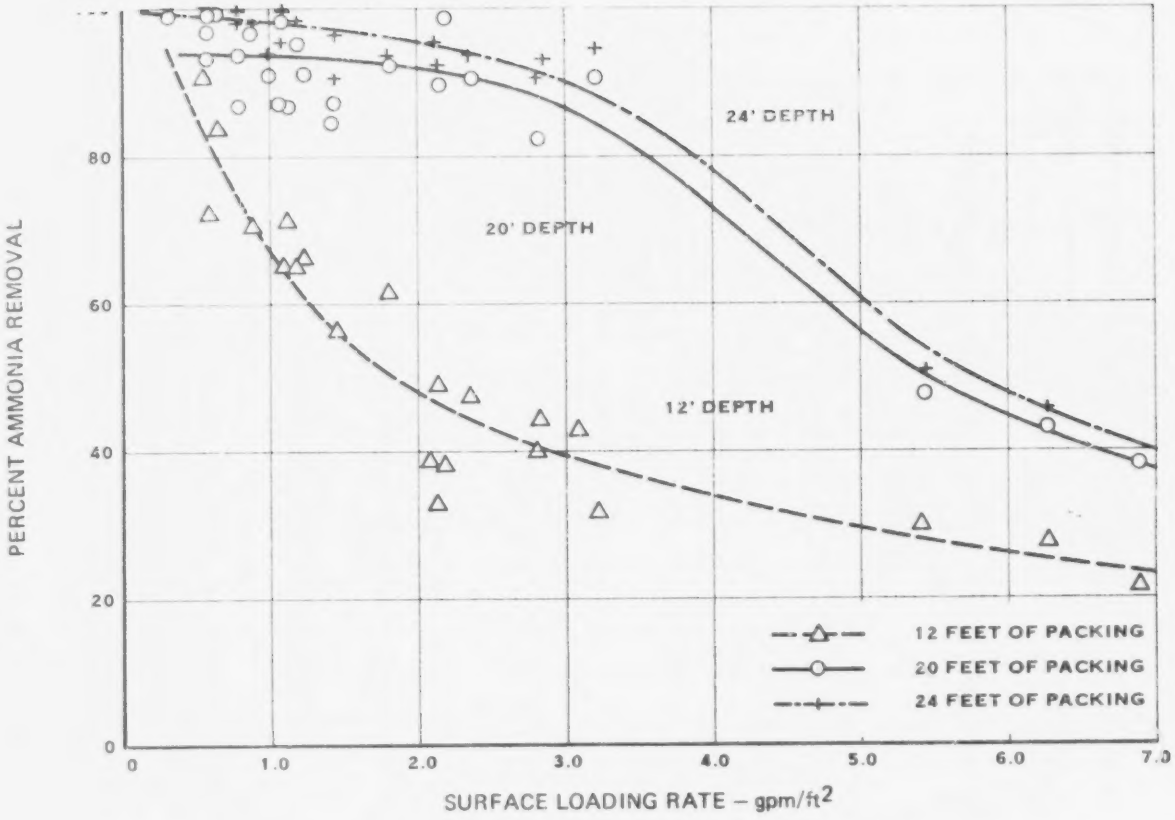

FIGURE 7

PERCENT AMMONIA REMOVAL VS SURFACE LOADING RATE
FOR VARIOUS DEPTHS OF PACKING

FIGURE 7

An open packing such as found in cooling towers was chosen over other types of packing such as Intalox^{R} saddles or Raschig rings in order to avoid high, expensive pressure losses and to utilize existing pilot plant data.

Temperature Requirements for Elution and Air Stripping

The choice of 23°C (74°F) as the elution water and air stripping temperatures was based on laboratory and pilot plant work by Battelle-Northwest. It was felt there was not enough data to accurately predict elution and air stripping requirements for lower or higher temperatures.

L.L. Ames showed that at 23°C (74°F) the elution rate probably represented an optimum between $Ca(OH)_2$ solubility in the eluting solution and the cation exchange kinetics.(1) He reported that zero degrees and 80°C represented the slowest elution rates, requiring 80 to 120 bed volumes.

If the laboratory work by Ames at low temperatures were used to design the proposed South Tahoe plant, the elution rate would be at least twice as long. For the proposed design flows at the longer elution rate, 15 ion exchange beds instead of 12 would be needed. The size of each exchange bed would be about the same. Nine beds would be in service and six in regeneration. Each elution tank and the tower recycle basin would have to be about 100% larger than required for 12 exchange beds.

The flow rate to the stripping tower would be about the same, however, for a 24-foot-high tower, about four times more surface area would be needed at the cooler temperatures. The fan would have to deliver nearly four times as much air.

The larger tower would also require greater maintenance expense for removal of calcium carbonate.

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(1) Ames, L.L. "Zeolitic Removal of Ammonium Ions From Agricultural Wastewaters," 13th Pacific Northwest Industrial Waste Conference Proceedings, 135,152, Washington State University. April 1967.

THE PROPOSED PLANT

Service Cycle

At a design capacity of 7.5 mgd, nine ion exchange beds would be in service at all times. The beds would be operated in parallel. When a total of 450 bed volumes (3.05 mg) had passed through three beds (150 bv per bed), these beds would be taken off line and three freshly regenerated beds would be put on line in their place. A flow totalizer would be used to measure the 150 bed volumes and automatically initiate an elution cycle.

Ion Exchange Beds

Drawing No. 4 shows a typical cross-section of an ion exchange bed. Each bed would be 12 feet in diameter and have an effective clinoptilolite depth of 8 feet. The flow through a bed would be six bed volumes per hour or 680 gpm. The surface loading rate would be 6 gallons per square foot per minute. Overdesign is about 20% due to choosing an integer (ft) diameter.

Due to calcium carbonate deposition during regeneration with pH 11+ lime solution, the inlet and outlet screens for each bed are removable for cleaning. The screens can be taken out of the bed without removing the clinoptilolite.

The beds have also been designed such that clinoptilolite can be added or removed by means of a water/clinoptilolite slurry. A special transfer header is included to aid in moving the clinoptilolite out of the bed and into the transfer line.

Clinoptilolite Transfer Tank

The transfer tank would be used for both washing and adding make-up clinoptilolite. To add make-up clinoptilolite, about 5% of an exchange bed volume could be dumped from bags into the transfer tank, washed if necessary, and then transferred to the top of any of the exchange beds in a slurry by pressurizing the transfer tank with water.

If clinoptilolite in an exchange bed required washing, it would be removed from the bottom by pressurizing an exchange vessel, put into slurry form, and moved to the transfer tank. After washing, the clinoptilolite would be returned in a slurry to the top of the exchange bed.

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Regeneration Cycle

At design flow the service cycle for a set of three beds would be about 25 hours. On the basis of nine beds in service and 25-hour service cycle, a set of beds would have to be regenerated about every 8 hours.

Under the elution procedure outlined earlier, the elution of ammonium ions would take place in two phases. Four bed volumes (81,600 gal.) would pass through a set of three beds for each phase; or a total of 8 bed volumes would be needed to completely elute the ammonium ion from each of the three exchange beds. Each elution phase would last about 4 hours. The elution would be upflow at a rate of 10 bed volumes per hour or 10 gallons per square foot per minute.

Two of the three 1,700-gpm pumps (Drawing No. 3) would be needed to provide enough flow to elute three exchange beds in parallel. The three pumps would be rotated so that one could be off line in order to remove lime build-up. After elution, one of the three pumps would be used to backwash the bed. Each bed would be washed upflow in sequence at a rate of 15 gpm/ft^2.

It is anticipated that most of the pipes, valves, and pumps, particularly those items which handle the lime elutrient, would have to be routinely cleaned. To facilitate cleaning of the pipes, all changes in direction would be made by using crosses with blind flanges. Wafer stock valves would be used in order that the pipe cleaning device would readily pass through the valve.

The regeneration cycle, as was the case for the service cycle, will be completely automatic.

Elutrient Storage Tanks

Three covered concrete elutrient storage tanks, each holding 94,500 gallons, or approximately 20% more than the anticipated elutrient volume, would be used.

The elutrient tanks would also function as settling basins for excess calcium carbonate. The tank floors have a 1-to-12 slope to a sludge draw-off sump. A slotted pipe is used to remove the elutrient in order to avoid disturbing the settled sludge. In the same manner, elutrient returning from the exchange beds flows into a stilling well before entering the tank.

Approximately a 4-hour period would elapse from the time ammonia-free elutrient returned from the stipping tower to the elutrient tank until it was needed for an elution polishing cycle. The return flow from the stripping tower would enter at the back of the tank and be used to move the settled solids toward the sludge sump. The 4-hour delay would allow time to clarify the elutrient. The rectangular tank design would permit, if necessary, the addition of mechanical sludge collection equipment.

Lime Storage and Feeders

At a design flow of 7.5 mgd, theoretically 2,300 lbs/day of calcium oxide would be required for elutrient make-up if the ion exchange beds were to remove 19 mg/l NH_3-N. If a 40% safety factor is included and the lime the District can purchase has a CaO content of 90% approximately 3,600 lbs of lime per day would be needed.

The proposed storage bin was sized to provide 10 to 14 days of storage.

About one-half of the ammonia is eluted from the exchange beds in the first hour regeneration. To meet this high demand for calcium hydroxide in the first hour, the lime feeder and slaker would have to be capable of handling about 800 lbs/hr. Two 800 lbs/hr feeder-slakers would be needed to allow for down-time for cleaning and maintenance.

Sodium Chloride Storage and Brine Feeder

Sodium chloride, 0.2 N, was found to be helpful during the elution of ammonia from the clinoptilolite. To make up 0.2N NaCl in the elutrient, 4,700 lbs/day would be needed, or on the basis of the proposed 2-week storage period, 66,000 lbs of sodium chloride would have to be stored.

Lime and Salt Mixing Basin

The mixing basin would be used for both the addition of calcium hydroxide and sodium chloride makeup and for initial clarification of the elutrient. The elutrient velocity through the basin would be about 0.1 ft/sec and the detention time about 9 minutes. The baffles within the basin would provide for 60 feet of linear flow distance. A hopper bottom would permit sludge draw-off.

Automatic pH monitoring equipment at the inlet and outlet to the basin would be used to control the lime feeder. The brine feeder would be paced by flow in the basin.

Ammonia Stripping Tower and Recycle Basin

The ammonia stripping tower has been sized to treat the contents of an elutrient tank in 8 hours, using two passes through the tower at 85% removal per pass. At a flow rate of 300 gpm, an air-to-water ratio of 300 cfm/gpm, and a loading of 3.5 gpm/ft^2, approximately 86 ft^2 of packing and 90,000 cfm air would be required.(1)

To prevent loss in stripping efficiency due to calcium carbonate build-up, the tower packing would be removable in sections for cleaning. The catch basin below the packing is sloped to the recycle basin below the tower to aid in sludge removal.

The design of the recycle basin below the tower would be similar to that of the elutrient tanks. A sloping bottom and sludge draw-off are included. The design is such that mechanical sludge collection could be added, if necessary, at a later date.

Process Controls

The selective ion exchange process has three basic operations, service cycle, regeneration cycle, and air stripping of the high ammonia regenerant. These operations occur simultaneously during normal operation of the process. The zeolite beds have four headers, bed influent and bed product, regenerant in and out, each header requiring a valve at each bed. During normal operation, nine beds are in service and three beds are in regeneration; when three beds are regenerated, they must be placed on line and three more beds taken off line for regeneration. This requires the opening or closing of 24 valves, plus the regenerant storage tank valves. While the bed regeneration is proceeding, the regenerant from the previous regeneration must be passed through the ammonia stripping tower twice. It is obvious the three basic operations must be automated with pneumatic or hydraulically actuated valves.

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(1) On the basis of processing 4 bv regenerant/required ion exchange bed volume, the tower is overdesigned by about 9%. On the basis of actual bed volume about 11% underdesign is indicated but this is an unrealistic basis because the beds are overdesigned. The tower should be more than adequate as specified.

In addition, to maintain the three-bed-regeneration sequence, a flow totalizer must be placed on a minimum of every third bed, and preferably on every bed, to record the number of bed volumes passed before regeneration is necessary. Also, each bed should have a flow rate recorder to maintain equal flows to each of the three beds.

After the three beds are regenerated, product water from the nine beds in service must be diverted and pumped through the three beds for backwashing. A flow controller must be placed on the product water to throttle the flow and divert the required supply of water for backwashing. Also, valves should be placed on the present carbon column effluent line or bed influent header and on the product to chlorination line to provide for bypassing of the ion exchange process, if necessary.

The regeneration backwash pumps and the tower pumps must be automated in one control center, since both elution and stripping operations will be proceeding at the same time.

Information obtained during pilot plant operation indicated the optimum temperature and pH to achieve maximum efficiency of the elution and stripping operations were at least 74°F and a pH of 11-11.5. Also, the presence of a significant amount of sodium increases the service cycle and shortens the elution cycle. In order to maintain optimum conditions, a pH monitoring system must be provided on the entrance and exit of the mixing basin to control lime slaker operation. The salt brine addition equipment must be automated in accordance with the flow through the mixing basin, to maintain an approximate .2 molar concentration in the regenerant. Temperature monitoring and controls must be placed immediately up stream of the zeolite beds and the stripping tower to maintain the optimum temperature in the regenerant for elution and stripping. In addition, the air utilized by the stripping tower must be maintained at the optimum temperature of 74°F. The air temperature monitoring and heat addition equipment must be automated to maintain optimum temperature conditions.

The accumulation of solids in the mixing basin, regenerant storage tanks, and the tower recycle basin will require daily pumping of sludge to the existing lime floc basin. Sludge pumping and the necessary valving can be accomplished manually.

In the pilot plant studies there was evidence of the zeolite "mudballing" with the cohesive solids in the regenerant. Manually operated valves have been provided to remove the zeolite from the bed, transfer the zeolite in a slurry to the transfer tank, wash it, and transfer it back to the bed.

During the initial start-up of the process, a large number of ammonia-nitrogen determinations will be required to determine a more accurate time period for the two elution cycles. When approximate time periods are established, the regeneration cycle can be placed on an automatic time basis, and should eliminate laboratory analysis except for periodic checks. Also, ammonia-nitrogen determinations will be required initially to verify the expected efficiency of the ammonia stripping tower, and the 150 bed volume service cycle before one mg/l ammonia-nitrogen breakthrough. After these design criteria are verified only the routine plant operation analysis will be required, except for periodic checking of decreased efficiency of the stripping tower as a result of calcium carbonate incrustation on the tower fill. Periodically the fill will be removed and cleaned.

Heating of Elutrient and Stripping Tower Air

In order to maintain both the elutrient and stripping tower air at 74°F, five separate heating systems would be needed.

The design has been based on utilizing the 500-gpm scrubber water off the exising lime and sludge furnaces to preheat the air to the tower. The remainder of the air heating would be accomplished with 180°F hot water from a new boiler. The heat would be transferred to the air by means of coils occupying a 7-foot-wide by 11-foot-high area on each end of the building opposite the open tower packing.

Three water-to-water heat exchangers would be used to heat the elutrient. Heat exchanger No. 1 would reheat to 74°F the elutrient going to the top of the stripping tower from either the elutrient storage tank or from the stripping tower recycle basin. Heat exchanger No. 2 would reheat the elutrient after it had made the second pass through the stripping tower but before it reached the elutrient storage tanks. The third heat exchanger, No. 3, would heat the elutrient to 74°F as it passed from a storage tank to an ion exchange bed during the elution cycle.

Sludge Collection

Ammonia removal studies were conducted with the mobile demonstration plant at the Richland wastewater treatment plant. From these studies it has been estimated that 0.4 lbs of dry solids per 1,000 gal of treated water would be generated. For the proposed process at the South Tahoe Water Reclamation Plant, approximately 3,300 lbs of dry solids would be produced per day.

The sludge would be pumped from the chemical mixing basin, each elutrient tank, and the stripping tower recycle basin through a 12-inch pipe to the existing lime flocculation basin. The 12-inch pipe would also be used to carry 1,700 gal per minute of backwash water from the final ion exchange bed rinse.

One 530-gpm sludge pump, operating for 15 minutes per day, would be used to pump the sludge to the floc basin. The high pump rate would be necessary in order to maintain scouring velocities in the 12-inch pipe. A second 530-gpm pump would be provided as a stand-by unit.

A new lime transfer pump at the existing chemical clarifier and a new centrifuge would be needed to handle the additional sludge.

FINANCIAL REQUIREMENTS

This section presents the estimated project costs and a brief summary of the required project financing.

Construction Cost Estimates

The construction cost estimates are based on the quantities and character of work described for each element of the project. Materials prices were obtained from manufacturers and were added to estimated labor costs plus contractors' overhead and profit, to obtain individual costs. These prices were then compared to actual bid prices for similar work, adjusted as necessary to reflect past experience in construction contract costs for the Lake Tahoe area. The estimates are based on construction starting in 1970. If the project is delayed then the cost estimates must be escalated to account for probable increases in material and labor costs. Table C is a detailed estimate of the project construction cost.

Incidental Cost Estimates

An allowance for incidental costs must be added to the construction cost. These costs are an integral part of the project cost and include engineering, construction inspection, administration of the project, and collection and publishing of operating data after completion of the project.

Operating Cost Estimates

Operation of the project will lead to increased costs for the District. Table D shows the estimated operating cost for the nitrogen removal plant when it is in complete operation. These costs are based on a design flow of 7.5 mgd and will be somewhat higher per millon gallons for flows less than the design capacity, since some of the costs are fixed. Labor costs are based on one operator per shift, 3 shifts per day, 365 days per year. Chemical costs are based on predicted dosages required for continuous operations. All prices are based on delivery to Tahoe. Electric power and natural gas costs are based on current rate schedules at Tahoe.

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Total Project Cost

The total estimated construction cost, including engineering and inspection, is $1,981,500. The average annual capital cost, amortized over 20 years at 6% interest, would be $172,700 per year. Based on a plant capacity of 7.5 mgd the capital cost per million gallons would be $63.10. The estimated annual operating cost is $232,100.

The data collection and publication phase upon completion and operation of the project is estimated to cost $72,000 per year, based on two engineers being assigned full time to the project.

TABLE C

ESTIMATED CAPITAL COSTS

DESCRIPTION	QUANTITY	UNIT	UNIT COST	TOTAL COST
Move-in		LS		$ 5,000.00
Bonds & Insurance		LS		2,000.00
Excavation & Backfill		LS		15,000.00
Concrete		LS		165,000.00
Steel Building		LS		65,000.00
Painting		LS		25,000.00
Welded Steel Pipe		LS		275,000.00
Large & Special Valves		LS		60,000.00
Misc. Fabricated Steel		LS		25,000.00
Floc Basin	1	ea	$30,000	30,000.00
Ion Exchange Beds	12	ea	27,000	324,000.00
Clinoptilotite	12,000	cf	10	120,000.00
Lime Storage & Slakers		LS		30,000.00
Salt Storage & Feeder		LS		30,000.00
Salt Conveyor		LS		20,000.00
Booster Pump	2	ea	4,500	9,000.00
Regenerant Pump	3	ea	5,000	15,000.00
Sludge Pump	2	ea	1,500	3,000.00
NH_3 Tower Pump	2	ea	1,500	3,000.00
NH_3 Tower Structure		LS		50,000.00
Boiler & Accessories		LS		24,000.00
Air Heat Exchanger		LS		8,000.00
Water Heat Exchangers		LS		8,000.00
Hot Water Pumps		LS		4,000.00
Electrical Work		LS		100,000.00
Instrumentation		LS		200,000.00
Heating & Ventilating		LS		15,000.00
Misc. Piping & Plumbing		LS		10,000.00
Operational Tests		LS		5,000.00
Cleanup		LS		2,000.00
TOTAL ESTIMATED CONTRACT PRICE				$1,647,000.00
Construction Contingencies				165,000.00
				$1,812,000.00
Design Engineering at 6.37%				115,500.00
Construction Inspection ($3,000/mo x 18 mos)				54,000.00
TOTAL ESTIMATED CAPITAL COST				$1,981,500.00

TABLE D

ESTIMATED OPERATION COSTS

	COST/YR	AT 7.5 mgd COST/mg
Makeup Lime	$ 19,900	$ 7.30
Makeup Sodium Chloride	18,900	6.90
Makeup Clinoptilolite	53,600	19.60
Operational Labor	50,800	18.60
Maintenance, Material & Labor	25,000	9.15
Chlorine	17,400	6.40
Natural Gas	20,300	7.40
Electricity	26,200	9.60
Total Operating Costs	$232,100	$ 84.95
Amortized Capital Cost (6% – 20 yr.)	172,700	63.10
TOTAL CAPITAL & OPERATING COST		$148.05

REQUESTED GRANT PROGRAM

General

The removal of nitrogen from sewage effluent remains as one of the most difficult problems to solve in the advanced waste treatment field. The various methods that have been tried at South Tahoe, both as pilot plant studies and full-scale operation, have not accomplished the complete removal of nitrogen that is necessary if sewage disposal in the Lake Tahoe basin is ever to be considered. The need for a complete nitrogen removal process is, of course, a national problem, not limited to Lake Tahoe only.

The proposed ion exchange process as envisioned in this report, gives promise of being a most satisfactory means of complete nitrogen removal. The pilot plant work that has been completed strongly indicates that ion exchange is effective, but also indicates that the process will be relatively expensive and also will be relatively sophisticated to properly operate.

The only assured means to adequately demonstrate the effectiveness of the process, will be to construct and operate a full-scale plant. Experience of South Tahoe with other elements of the advanced waste treatment process has clearly shown that full plant operation is the only effective means for demonstrating performance. Pilot plant studies, while necessary and effective, do not give the proof that the process can be operated on a continuous daily basis and that the process can work within the limits of dependability and operating limitations imposed by full-scale plants.

Therefore, the South Tahoe Public Utility District strongly believes that the effectiveness of the proposed ion exchange process for nitrogen removal can be proven only by constructing and operating a full-scale 7½-mgd capacity plant. Construction and operation of the full-scale plant will make available complete, accurate, and dependable information on nitrogen removal and will demonstrate that the operation can be done on a continuous, effective basis. Such information will be of inestimable value in the coming decade, when the water quality control program will be instigated on a nation-wide basis.

It is only logical that the ion exchange plant be constructed at South Tahoe, since the District has available the only full-scale operating advanced wastewater treatment plant in the nation along with the trained, skilled operating personnel required to operate the ion exchange plant, and also has available through its manager and engineering consultants, the technical experience and expertise to make the design, construction, and operation phases a success.

Proposed Schedule

The design of the full-scale plant can be initiated immediately upon approval being given by FWQA. The design can be completed within a 6-month period and construction bids can be obtained within 30 days after approval of these final plans.

The District will utilize its consulting engineers, Clair A. Hill & Associates, to accomplish the design. The consultants will be associated with Cornell, Howland, Hayes and Merryfield Consulting Engineers of Corvallis, Oregon, during the design and operation of the ion exchange plant. These consultants have previously designed, supervised construction, and trained the operating personnel for the District's advanced waste treatment plant.

The construction of the plant will require approximatley 9 months on an accelerated schedule. A one-year construction period would be advisable in order not to pay a premium for earlier completion. Construction would be done through a public bidding procedure and the contract would be awarded to the lowest responsible bidder. Inspection of the construction, to assure compliance with the approved plans and specifications, would be done by the District's consulting engineers.

Allowing adequate time for review of this report, design of the final plant, and construction of the plant, indicates that operation could begin sometime during the spring of 1972. Since the proposed process is new and untried, an operating and data collection program extending over a 2-year period is recommended. This would mean that the final project report would be submitted in 1977.

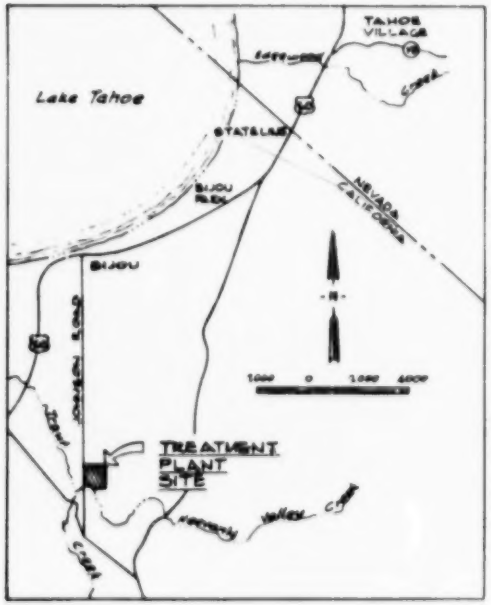
Project Grant Costs

The proposed project as outlined here would be financed entirely by grant funds from the FWQA. The District would make available its advanced waste treatment plant, laboratory facilities, and administrative offices to the project. In addition, the District Manager, Russell L. Culp, would serve as the Grant Project Director at no charge to the project.

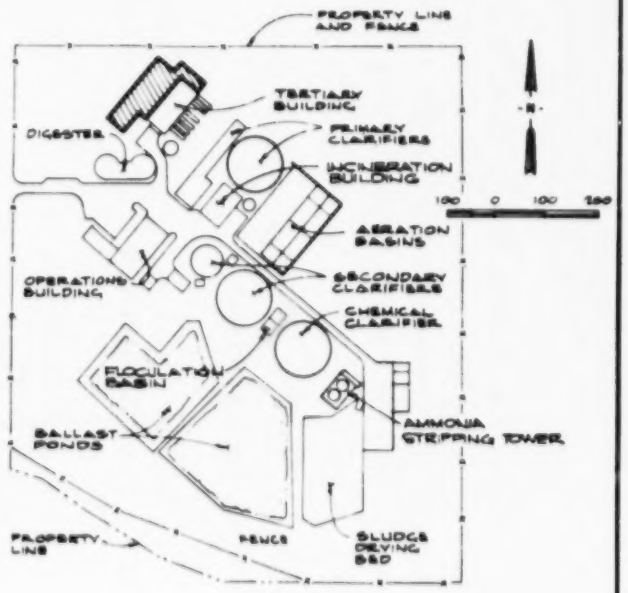
Financial requirements for the grant would therefore need to be disbursed by the FWQA in accordance with the following schedule:

FISCAL YEAR	DESCRIPTION OF WORK	GRANT AMOUNT
1970-71	Engineering Design	$115,500
1970-71	Construction & Inspection	927,000
1971-72	Construction & Inspection	939,000
1972 thru 1977	Operation & Data Collection	323,000/yr

The above costs are requested to be paid by the FWQA under a continuing grant program.

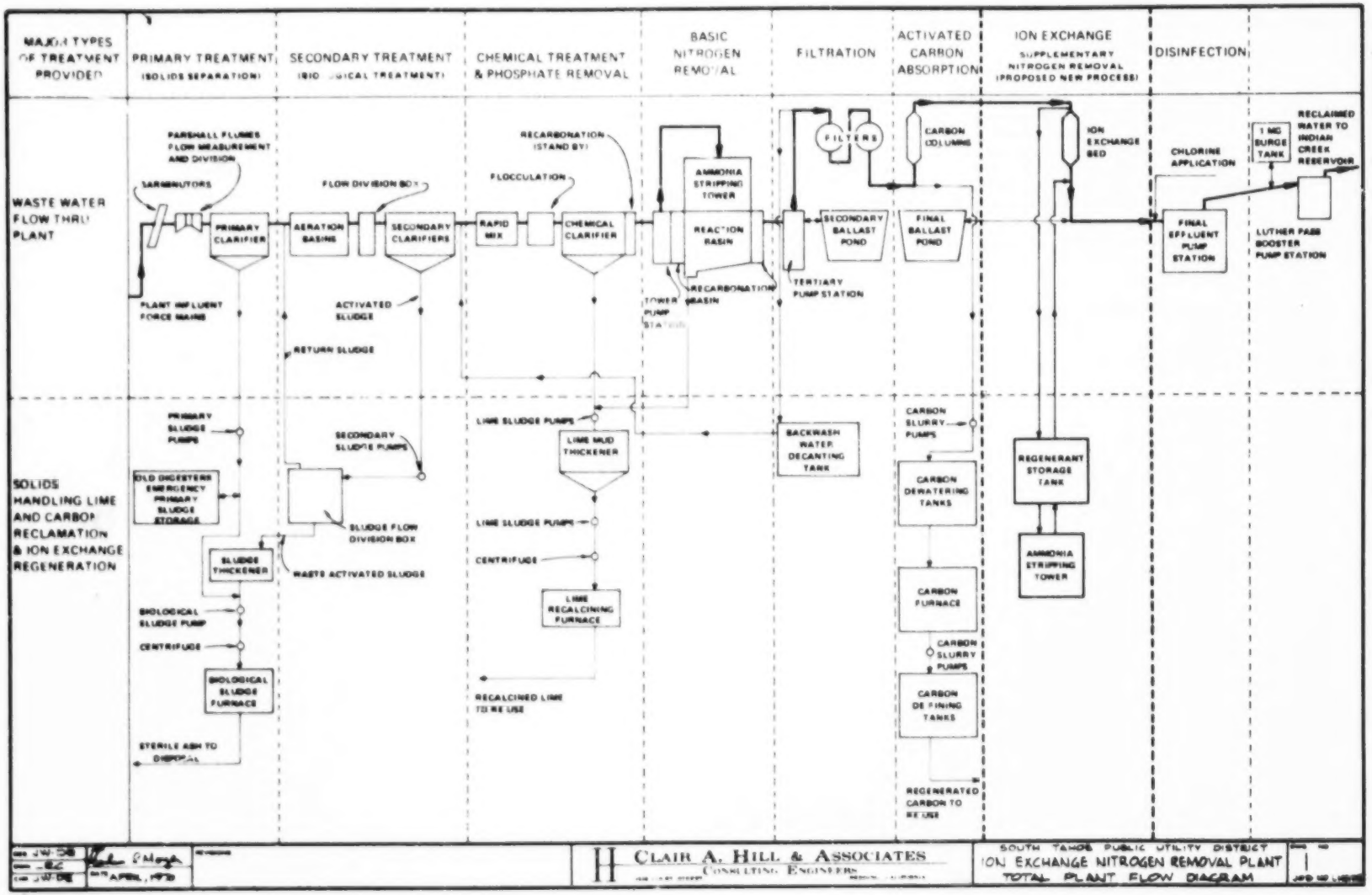


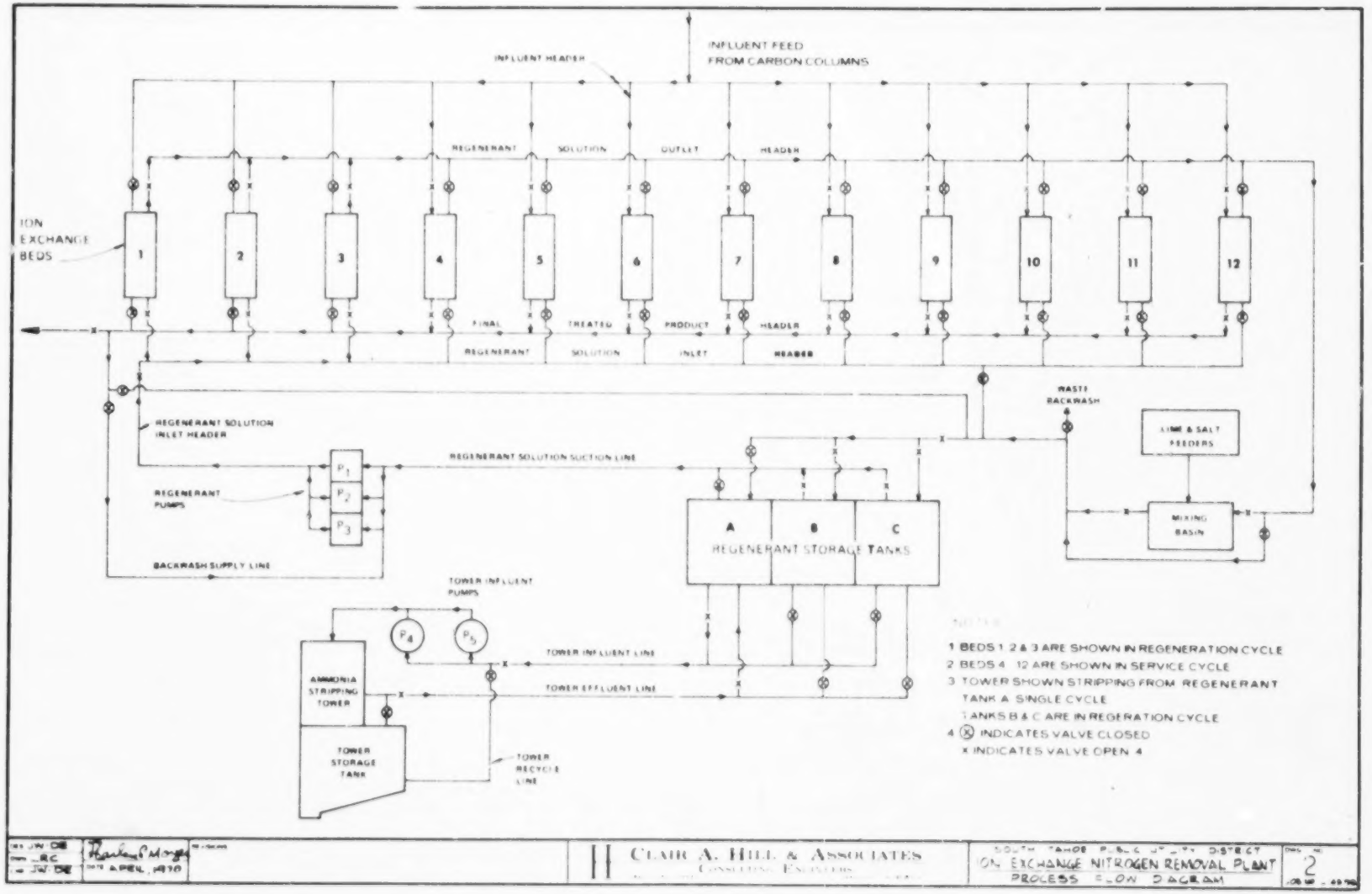
VICINITY MAP



LOCATION PLAN

	CLAIR A. HILL & ASSOCIATES, CONSULTING ENGINEERS	SOUTH TAHOE PUBLIC UTILITY DISTRICT ION EXCHANGE NITROGEN REMOVAL PLANT VICINITY MAP & LOCATION PLAN	L-165-28


MAJOR TYPES OF TREATMENT PROVIDED
PRIMARY TREATMENT (SOLIDS SEPARATION)
SECONDARY TREATMENT (BIOLOGICAL TREATMENT)
CHEMICAL TREATMENT & PHOSPHATE REMOVAL
BASIC NITROGEN REMOVAL
FILTRATION
ACTIVATED CARBON ABSORPTION
ION EXCHANGE
SUPPLEMENTARY NITROGEN REMOVAL (PROPOSED NEW PROCESS)
DISINFECTION
WASTE WATER FLOW THRU PLANT
SOLIDS HANDLING LIME AND CARBON RECLAMATION & ION EXCHANGE REGENERATION
PARSHALL FLUMES FLOW MEASUREMENT AND DIVISION
COMMINUTORS
PRIMARY CLARIFIER
PLANT INFLUENT FORCE MAINS
AERATION BASINS
FLOW DIVISION BOX
SECONDARY CLARIFIERS
ACTIVATED SLUDGE
RETURN SLUDGE
RAPID MIX
FLOCCULATION
RECARBONATION (STAND BY)
CHEMICAL CLARIFIER
AMMONIA STRIPPING TOWER
REACTION BASIN
RECARBONATION BASIN
TOWER PUMP STATION
FILTERS
SECONDARY BALLAST POND
TERTIARY PUMP STATION
CARBON COLUMNS
FINAL BALLAST POND
ION EXCHANGE BED
CHLORINE APPLICATION
FINAL EFFLUENT PUMP STATION
1 MG SURGE TANK
LUTHER PASS BOOSTER PUMP STATION
RECLAIMED WATER TO INDIAN CREEK RESERVOIR
PRIMARY SLUDGE PUMPS
OLD DIGESTERS EMERGENCY PRIMARY SLUDGE STORAGE
SECONDARY SLUDGE PUMPS
SLUDGE FLOW DIVISION BOX
WASTE ACTIVATED SLUDGE
SLUDGE THICKENER
BIOLOGICAL SLUDGE PUMP
CENTRIFUGE
BIOLOGICAL SLUDGE FURNACE
STERILE ASH TO DISPOSAL
LIME SLUDGE PUMPS
LIME MUD THICKENER
LIME SLUDGE PUMPS
CENTRIFUGE
LIME RECALCINING FURNACE
RECALCINED LIME TO RE USE
BACKWASH WATER DECANTING TANK
CARBON SLURRY PUMPS
CARBON DEWATERING TANKS
CARBON FURNACE
CARBON SLURRY PUMPS
CARBON DE FINING TANKS
REGENERATED CARBON TO RE USE
REGENERANT STORAGE TANK
AMMONIA STRIPPING TOWER
APRIL, 1970
CLAIR A. HILL & ASSOCIATES
CONSULTING ENGINEERS
SOUTH TAHOE PUBLIC UTILITY DISTRICT
ION EXCHANGE NITROGEN REMOVAL PLANT
TOTAL PLANT FLOW DIAGRAM
1



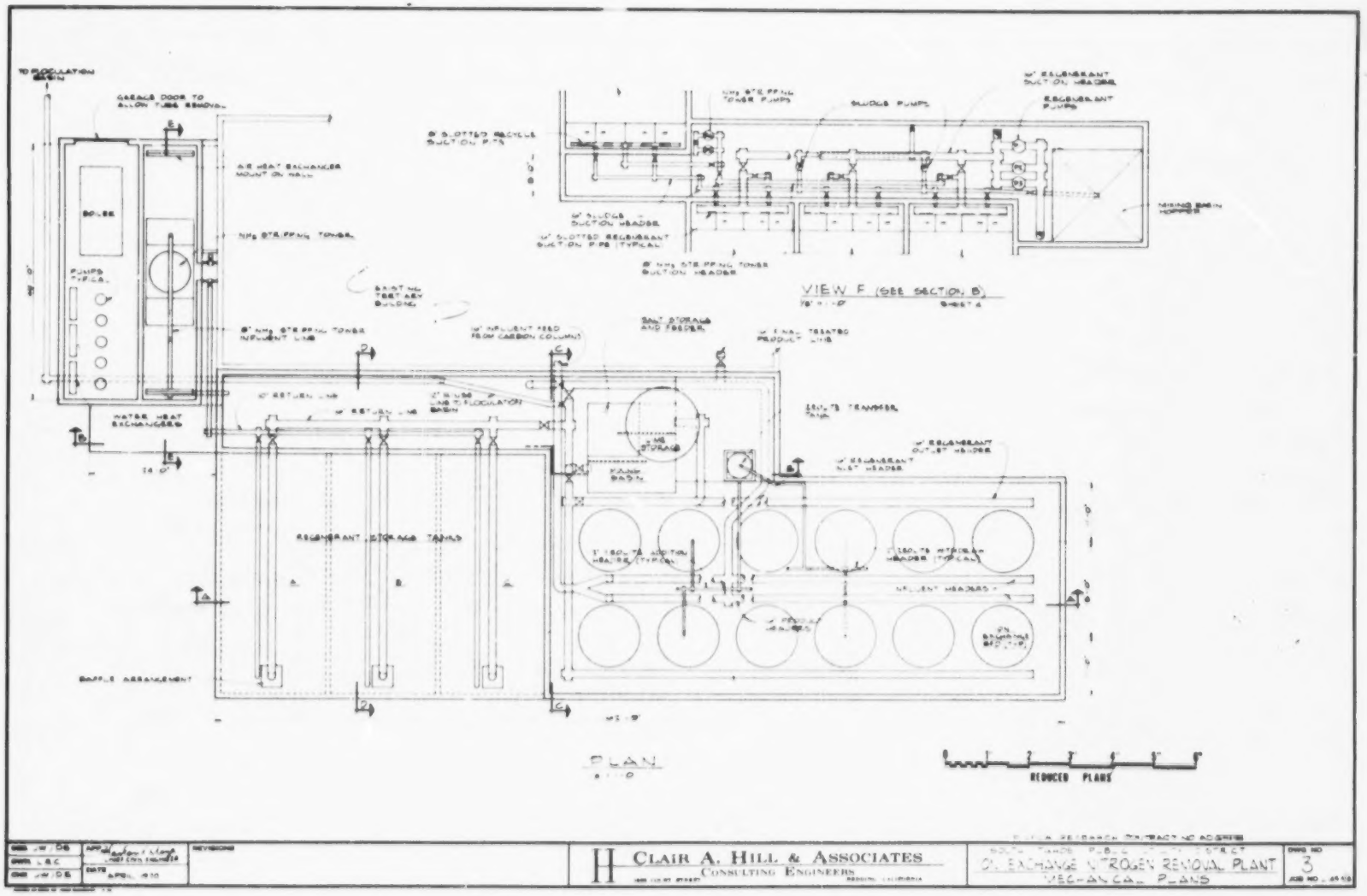
DES JW DE
DRN RC
CK JW DE

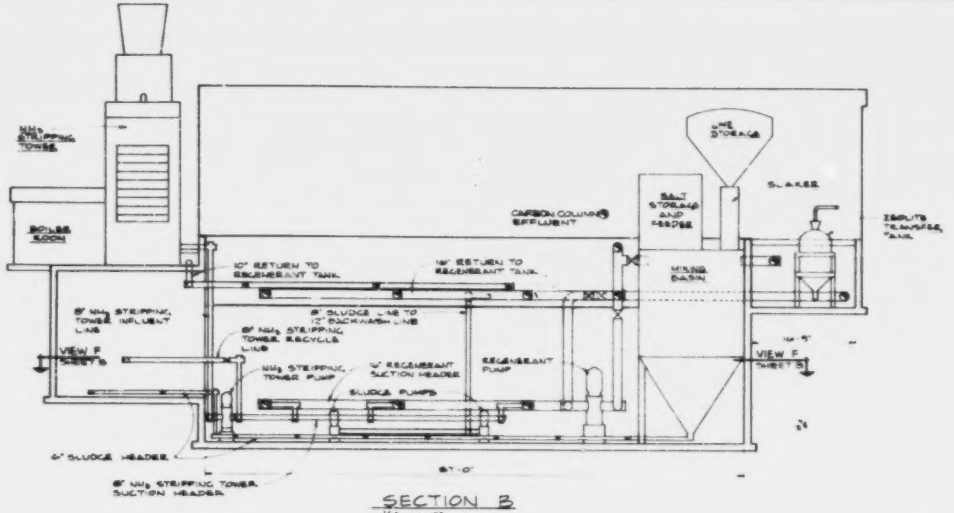
Harley S Morgan
DATE APRIL 1970

CLAIR A. HILL & ASSOCIATES
CONSULTING ENGINEERS

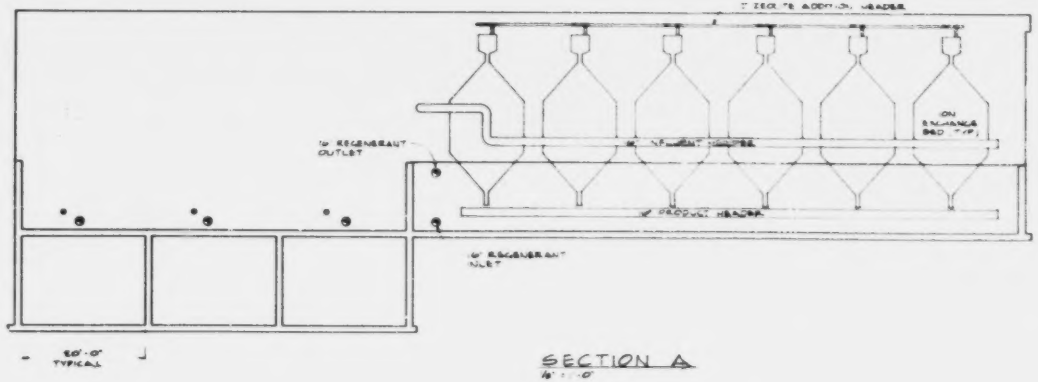
SOUTH TAHOE PUBLIC UTILITY DISTRICT
ION EXCHANGE NITROGEN REMOVAL PLANT
PROCESS FLOW DIAGRAM

DWG NO 2


VIEW F (SEE SECTION B)
PLAN
REDUCED PLANS
CLAIR A. HILL & ASSOCIATES
CONSULTING ENGINEERS
ION EXCHANGE NITROGEN REMOVAL PLANT
MECHANICAL PLANS
3



SECTION B
3/8" = 1'-0"



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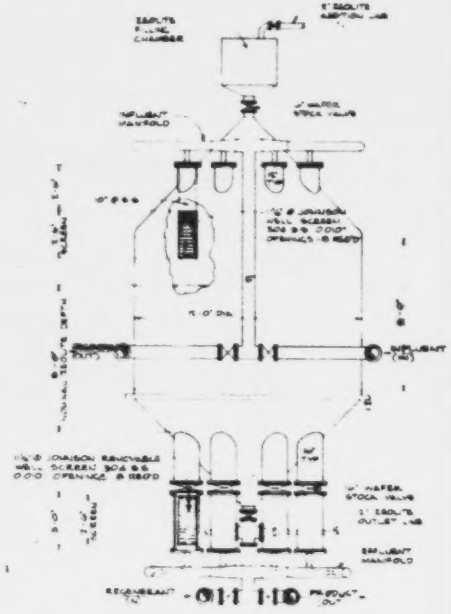


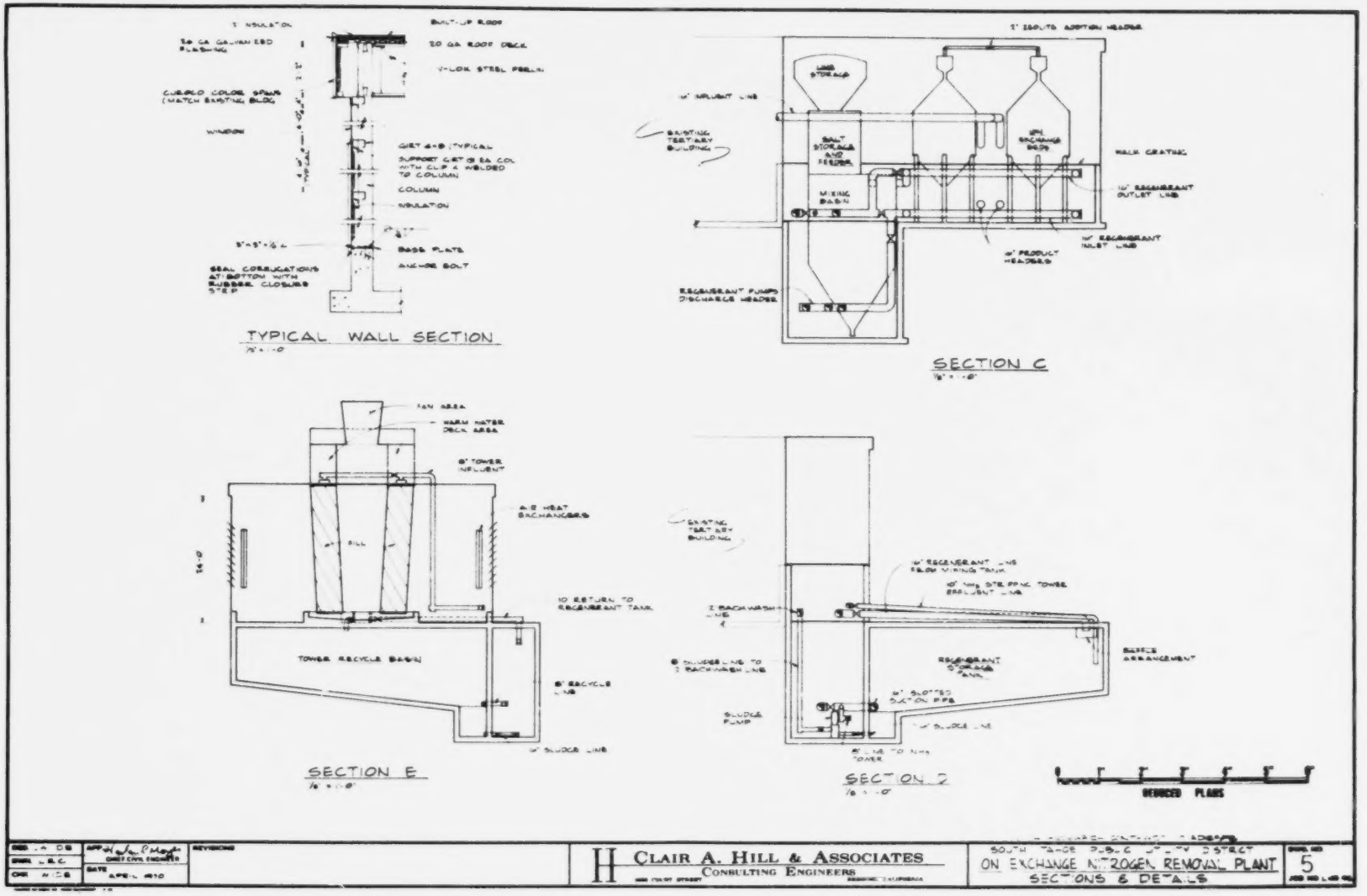
TYPICAL ION EXCHANGE BED
NO SCALE

REDUCED PLANS

DES. JW/DB	APP.	REVISIONS	H CLAIR A. HILL & ASSOCIATES CONSULTING ENGINEERS REDDING, CALIFORNIA
DRWN. L.E.C.	CHIEF CIVIL ENGINEER		
CHK. JW/DB	DATE APRIL 1970		

USPHS RESEARCH CONTRACT NO. WP-00748
SOUTH TAHOE PUBLIC UTILITY DISTRICT
ION EXCHANGE NITROGEN REMOVAL PLANT
SECTIONS & DETAILS

DRWG. NO. 4
JOB NO. 67-140


TYPICAL WALL SECTION
SECTION C
SECTION E
SECTION 2
CLAIR A. HILL & ASSOCIATES
CONSULTING ENGINEERS
ON EXCHANGE NITROGEN REMOVAL PLANT
SECTIONS & DETAILS
5

1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
W	05D	

5 Organization

Battelle-Northwest, Richland, Washington 99352
South Tahoe Public Utility District, South Lake Tahoe, California 95705

6 Title

WASTEWATER AMMONIA REMOVAL BY ION EXCHANGE

10 Author(s)

16 Project Designation

EPA Project #17010 ECZ

21 Note

22 Citation

23 Descriptors (Starred First)

*Waste Treatment, *Ammonia, *Ion Exchange, *Electrolysis, *Cost Comparisons, Sewage, Sewage Effluents, Municipal Wastes, Waste Water (Pollution), Nitrogen Compounds, Cation Exchange, Zeolites, Separation Techniques, Air-Water Interfaces, Cost Analysis, Design, Design Criteria

25 Identifiers (Starred First)

*Clinoptilolite, *Stripping, Air Stripping

27 Abstract

Pilot plant investigations were conducted on the ion exchange removal of ammonia-nitrogen from clarified and carbon-treated secondary effluents and from clarified raw sewage. The ion exchange process utilized clinoptilolite, a natural zeolite. Average ammonia removals from low magnesium wastewaters were in the range of 93% to 97%. With a wastewater Mg concentration of 20 mg/l, solids formation presented problems but they appear surmountable. The primary method used for regenerant renovation was air stripping with which a 2N regenerant at a pH of 11.5 is recommended. Electrolytic regenerant renovation using a neutral solution that is less prone to solids formation was also piloted during the project.

Two process designs are included giving cost estimates for ion exchange ammonia removal from tertiary effluent. With capital costs amortized at 6% for 20 years, the total cost to remove ammonia from 1000 gal. of tertiary effluent is 14.8¢ for a 7.5 mgd plant using regenerant air stripping and 12.7¢ for a 10 mgd plant using electrolytic regenerant renovation. The 7.5 mgd design was prepared by South Tahoe Public Utility District under EPA Project Number 17010 EEZ and is included for convenience. Other work discussed in the report was performed by Battelle-Northwest under EPA Project Number 17010 ECZ. (Mercer - Battelle-Northwest)

Abstractor: Basil W. Mercer, Jr.
Institution: Battelle-Northwest

WR:102 (REV. JULY 1969)
WRSIC

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WASHINGTON, D. C. 20240

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